PATENT ABSTRACTS OF JAPAN

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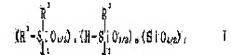
(54) DIORGANOPOLYSILOXANE AND ITS PRODUCTION

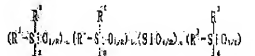
(57)Abstract:

PURPOSE: To produce diorganopolysiloxane which can give a cured organic resin excellent in mold release, weathering resistance and flexibility by subjecting a specified polyorganosiloxane, an organic compound containing epoxy groups and aliphatic unsaturations and diorganopolysiloxane to an addition reaction in the presence of a platinum catalyst.



I

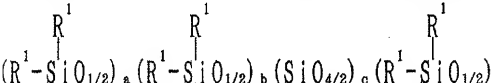
CONSTITUTION: An organopolysiloxane (A) of formula I (wherein R1 is a monovalent hydrocarbon group except alkenyl ; d is 0 or a positive integer; e and f are positive numbers; d/f is 0-4; e/f is 0.05-4; and (d+e)/f is 0.2-4), an organic compound (B) containing an epoxy group and an aliphatic unsaturation bond, an alkenyl-terminated diorganopolysiloxane (C),and an arbitrary amount of an alkoxysilylalkene (D) are subjected to an addition reaction in the presence of a platinum catalyst to effect the addition reaction of at least one mol of the aliphatic unsaturation bonds of components B and C with one mol of the Si-H bonds of component A to obtain an epoxyorganopolysiloxane-residue- containing diorganopolysiloxane of formula II (wherein R2 is H or R1; and R3 is an epoxy organic group or the like).



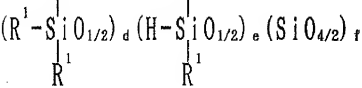
II

CLAIMS

[Claim(s)]
[Claim 1]To chain both ends, it is a general formula. :[Formula 1]



{R^1 is a monovalent hydrocarbon group except an alkenyl group among a formula, and R^2 is the monovalent hydrocarbon group or hydrogen atom except an alkenyl group, R^3 An epoxy group content organic group or an alkoxy silyl alkyl group, However, at least one in R^3 is an epoxy group content organic group, R^4 is a bivalence hydrocarbon group, and a is 0 or a positive number, b is a positive number, and c is a positive number, and a/c is a positive number of 0-4, b/c is a positive number of 0.05-4, and (a+b)/c is a positive number of 0.2-4. Diorganopolysiloxane which has the epoxy group content organopolysiloxane residue expressed with}.
[Claim 2](A) The bottom of existence of a platinum system catalyst, the (B) general formula : [Formula 2]



{R^1 is a monovalent hydrocarbon group except an alkenyl group among a formula, and d is 0 or a positive number, e is a positive number, and f is a positive number, and d/f is a positive number of 0-4, e/f is a positive number of 0.05-4, and (d+e)/f is a positive number of 0.2-4. Organopolysiloxane expressed with}, an organic compound which has the (C) epoxy group and aliphatic unsaturated bonds, (D) An addition of a diorganopolysiloxane {ingredient and (D) ingredient which has an alkenyl group in chain both ends is a quantity from which the number of mols of aliphatic unsaturated bonds included in the (C) ingredient and the (D) ingredient to 1 mol of silicon atom absorbed water matter atoms in the (B) ingredient becomes more than the equivalent. [(C)] A manufacturing method of the diorganopolysiloxane according to claim 1 carrying out the addition reaction of the alkoxy silylalkene of} and the (E) arbitrary dose.

[Translation done.]

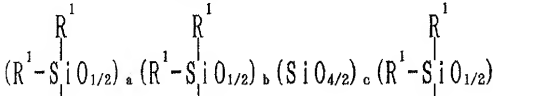
DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application]This invention relates to new diorganopolysiloxane and a manufacturing method for the same which have epoxy group content organopolysiloxane residue in chain both ends in detail about diorganopolysiloxane and a manufacturing method for the same.
[0002]
[Description of the Prior Art]The diorganopolysiloxane which has an epoxy group, By blending with thermosetting organic resin, such as an epoxy resin and phenol resin, the characteristics which are the features of diorganopolysiloxane, such as a mold-release characteristic, weatherability, and pliability, can be given to hardening organic resin after hardening, and the internal stress of this hardening organic resin can be eased further.
[0003]As diorganopolysiloxane which has such an epoxy group, For example, the diorganopolysiloxane (refer to JP,2-69528,A) which has an epoxy group in diorganopolysiloxane (refer to JP,61-60726,A) or chain both ends which has an epoxy group in a chain side chain is proposed.
[0004]
[Problem(s) to be Solved by the Invention]However, the diorganopolysiloxane proposed by JP,61-60726,A, When the reactivity of the epoxy group which it has in the chain side chain is low and this is blended with thermosetting organic resin, such as an epoxy resin and phenol resin, by the unreacted epoxy group in diorganopolysiloxane. The diorganopolysiloxane which there is a problem that the physical property of the obtained hardening organic resin changes temporally, and was proposed by JP,2-69528,A had the problem that the epoxy group in a monad was limited to two pieces.
[0005]this invention person reached this invention, as a result of trying hard wholeheartedly, in order to solve the above-mentioned problem.

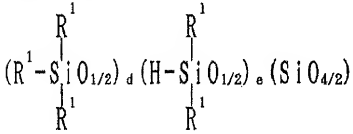
[0006]That is, the purpose of this invention is to provide new diorganopolysiloxane and a manufacturing method for the same which have epoxy group content organopolysiloxane residue in chain both ends.

[0007]

[The means for solving a problem, and its operation] This invention is a general formula to chain both ends. : [Formula 3]



{R^1 is a monovalent hydrocarbon group except an alkenyl group among a formula, and R^2 is the monovalent hydrocarbon group or hydrogen atom except an alkenyl group, R^3 An epoxy group content organic group or an alkoxy silyl alkyl group, However, at least one in R^3 is an epoxy group content organic group, R^4 is a bivalence hydrocarbon group, and a is 0 or a positive number, b is a positive number, and c is a positive number, and a/c is a positive number of 0-4, b/c is a positive number of 0.05-4, and (a+b)/c is a positive number of 0.2-4. The bottom of existence of the diorganopolysiloxane which has the epoxy group content organopolysiloxane residue expressed with}, and (A) platinum system catalyst, (B) general formula : [Formula 4]



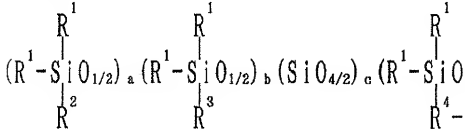
{R^1 is a monovalent hydrocarbon group except an alkenyl group among a formula, and d is 0 or a positive number, e is a positive number, and f is a positive number, and d/f is a positive number of 0-4, e/f is a positive number of 0.05-4, and (d+e)/f is a positive number of 0.2-4. The organopolysiloxane expressed with}, the organic compound which has the (C) epoxy group and aliphatic unsaturated bonds, (D) The addition of the diorganopolysiloxane which has an alkenyl group in chain both ends, and {ingredient and (D) ingredient is a quantity from which the number of mols of the aliphatic unsaturated bonds included in the (C) ingredient and the (D) ingredient to 1 mol of silicon atom absorbed water matter atoms in the (B) ingredient becomes more than the equivalent. [(C)] It is related with the manufacturing method of the

diorganopolysiloxane carrying out the addition reaction of the alkoxy silylalkene of} and the (E) arbitrary dose.

[0008]First, diorganopolysiloxane of this invention is explained in detail.

[0009]Diorganopolysiloxane of this invention is a general formula to chain both ends. :

[Formula 5]

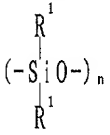


It comes out and has the epoxy group content organopolysiloxane residue expressed. R^1 is a monovalent hydrocarbon group except an alkenyl group among an upper type, and specifically, Aryl groups, such as cycloalkyl group; phenyl groups, such as alkyl group; cyclopentylic groups, such as a methyl group, an ethyl group, a propyl group, a butyl group, a pentyl group, and a hexyl group, a cyclohexyl group, and a cycloheptyl group, a tolyl group, and a xylyl group; Benzyl, a phenethyl group, Aralkyl groups, such as a phenylpropyl group; monovalent hydrocarbon groups, such as substituted alkyl groups, such as a chloromethyl group and a 3,3,3-trifluoropropyl group, are illustrated. R^2 is the monovalent hydrocarbon group or hydrogen atom except an alkenyl group, and, specifically, the same monovalent hydrocarbon group as the above is illustrated as a monovalent hydrocarbon group of R^2. R^3 is an epoxy group content organic group or an alkoxy silyl alkyl group, however at least one in R^3 is an epoxy group content organic group. As an epoxy group content organic group of R^3, specifically, Epoxy group content organic groups, such as a glycidoxy ethyl group, a glycidoxy propyl group, and a 3,4-epoxycyclohexyl ethyl group, are illustrated, and as an alkoxy silyl alkyl group of R^3, Specifically, alkoxy silyl alkyl groups, such as a trimethoxysilyl ethyl group, a trimethoxysilylpropyl group, a dimethoxymethyl silylpropyl group, a methoxy dimethylsilyl propyl group, a triethoxy silyl ethyl group, and a tripropoxy silylpropyl group, are illustrated. R^4 is a bivalence hydrocarbon group and, specifically, a methylmethylene group, ethylene, a methyl ethylene group, a propylene group, a butylene group, a pentylene group, etc. are illustrated. Diorganopolysiloxane of this invention is combined with the above-mentioned epoxy group content organopolysiloxane residue via an R^4 group.

[0010]a is 0 or the positive number which shows the number of the monofunctional siloxane units (M unit) which have the monovalent hydrocarbon group or silicon atom absorbed water matter atom except an alkenyl group among an upper type, b is a positive number which

shows the number of the monofunctional siloxane units (M unit) which have an epoxy group content organic group or an alkoxy silyl alkyl group, c is a positive number which shows the number of tetrafunctional siloxane units (Q unit), each ratio and a/c are the positive numbers of 0-4, and b/c is a positive number of 0.05-4, and (a+b)/c is a positive number of 0.2-4. Monofunctional siloxane units (M unit) cannot have this [good] for four pieces to one tetrafunctional siloxane units (Q unit), and diorganopolysiloxane of this invention receives thermosetting organic resin, it is because the monofunctional siloxane units (M unit) which have an epoxy group content organic group or an alkoxy silyl alkyl group need to be at least 0.05 piece in order to excel in a stress release effect and compatibility.

[0011]Although diorganopolysiloxane of this invention has epoxy group content organopolysiloxane residue in chain both ends, diorganopolysiloxane in particular of a principal chain part is not limited, for example, it is a general formula. : [Formula 6]



It comes out and the diorganopolysiloxane expressed is mentioned. R^1 is a monovalent hydrocarbon group except an alkenyl group among an upper type, and, specifically, said same monovalent hydrocarbon group is illustrated. As for n, although n is a positive number which shows the degree of polymerization of diorganopolysiloxane which is a main chain among an upper type and it is not limited in particular, in order for diorganopolysiloxane of this invention to be excellent in a stress release effect and compatibility to thermosetting organic resin, it is preferred that it is the range of 1-500. As diorganopolysiloxane of such a principal chain part, specifically, Dimethylpolysiloxane, a methylethyl polysiloxane, Diorganopolysiloxane, such as a methylphenyl polysiloxane, a dimethylsiloxane methylphenyl siloxane copolymer, a dimethylsiloxane diphenyl siloxane copolymer, and a diphenylpolysiloxane, is illustrated.

[0012]At a room temperature, diorganopolysiloxane of this invention is liquefied or a solid state.

Although the molecular weight in particular is not limited, when this is blended with thermosetting organic resin, such as an epoxy resin and phenol resin, since compatibility with this organic resin is good, it is preferred [the molecular weight of diorganopolysiloxane of this invention] that it is the range of 500-1,000,000.

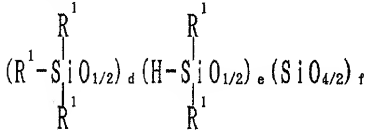
[0013]Below, the manufacturing method of diorganopolysiloxane of this invention is explained.

[0014]In the manufacturing method of this invention, the platinum system catalyst of the (A)

ingredient is a catalyst for carrying out the addition reaction of the aliphatic unsaturated bonds in the silicon atom absorbed water matter atom in the (B) ingredient, the (C) ingredient, the (D) ingredient, and the (E) ingredient. (A) The platinum system catalyst of an ingredient will not usually be limited, especially if used as a hydrosilylation addition reaction catalyst. Specifically as a platinum system catalyst of such a (A) ingredient, the activated carbon of the alcohol solution of chloroplatinic acid and chloroplatinic acid, the complex of platinum and unsaturation aliphatic hydrocarbon, the complex of platinum and a vinyl siloxane, platinum black, and platinum support, etc. are illustrated. In the manufacturing method of this invention, the addition in particular of the (A) ingredient is not limited, but is the usual catalyst amount, and, specifically, it is preferred that it is the range of 0.01-500 ppm as platinum metal in the (A) ingredient to the (B) ingredient.

[0015]It is an ingredient for introducing the organopolysiloxane residue which combines organopolysiloxane of the (B) ingredient with the chain both ends of diorganopolysiloxane of this invention in the manufacturing method of this invention, and is a general formula. :

[Formula 7]



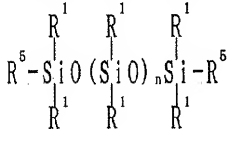
It is come out and expressed. R^1 is a monovalent hydrocarbon group except an alkenyl group among an upper type, and specifically, Aryl groups, such as cycloalkyl group; phenyl groups, such as alkyl group; cyclopentylic groups, such as a methyl group, an ethyl group, a propyl group, a butyl group, a pentyl group, and a hexyl group, a cyclohexyl group, and a cycloheptyl group, a tolyl group, and a xylyl group; Benzyl, a phenethyl group, Aralkyl groups, such as a phenylpropyl group; monovalent hydrocarbon groups, such as substituted alkyl groups, such as a chloromethyl group and a 3,3,3-trifluoropropyl group, are illustrated. d is 0 or the positive number which shows the number of the monofunctional siloxane units (M unit) which have a monovalent hydrocarbon group except an alkenyl group, e is a positive number which shows the number of the monofunctional siloxane units (M unit) which have a silicon atom absorbed water matter atom, f is a positive number which shows the number of tetrafunctional siloxane units (Q unit), each ratio and d/f are the positive numbers of 0-4, and e/f is a positive number of 0.05-4, and (d+e)/f is a positive number of 0.2-4. This cannot have eight M of monofunctional siloxane-units unit [good] for four pieces to one tetrafunctional siloxane units (Q unit), it is because the monofunctional siloxane units (M unit) which have a silicon atom absorbed water

matter atom need to be at least 0.05 piece in order for diorganopolysiloxane of this invention to have reactivity to thermosetting organic resin and to be excellent in compatibility.

[0016]Such organopolysiloxane of the (B) ingredient can be conventionally manufactured by the well-known method. (B) How to specifically carry out the cohydrolysis of a tetra halo silane and the mono- halo silane as a manufacturing method of an ingredient, The method of carrying out the cohydrolysis of tetra alkoxysilane and the mono- alkoxysilane, the method of hydrolyzing and re-equilibration polymerizing tetra alkoxysilane and tetra ORGANO disiloxane, etc. are illustrated, and preferably in a hydrochloric acid aqueous solution, It is the method (refer to JP,61-195129,A) of trickling tetra alkoxysilane, stirring the organic silicon compound chosen from the group which consists of hexa ORGANO disiloxane, tetra ORGANO disiloxane, a trio luganot halo silane, and a JIORUGANO halo silane.

[0017]In the manufacturing method of this invention, the organic compound which has the epoxy group and aliphatic unsaturated bonds of the (C) ingredient is an ingredient for introducing an epoxy group content organic group into organopolysiloxane residue. (C) As an organic compound which it has, the epoxy group and aliphatic unsaturated bonds of an ingredient specifically, Vinyl glycidoxy ether, allyl glycidoxy ether, Butenyl glycidoxy ether, 1,2-epoxy-4-vinylcyclohexane, 2,3-epoxy-5-vinyl norbornene, 1,2-epoxy-1-methyl-4-isopropenylcyclohexane, etc. are illustrated.

[0018]In the manufacturing method of this invention, diorganopolysiloxane of the (D) ingredient is an ingredient which forms the main chain of diorganopolysiloxane of this invention. Specifically, especially diorganopolysiloxane of such a (D) ingredient is a general formula, although not limited. : [Formula 8]



(R^1 is a monovalent hydrocarbon group except an alkenyl group among a formula, R^5 is an alkenyl group, and n is a positive number.) -- it is expressed. R^1 is a monovalent hydrocarbon group except an alkenyl group among an upper type, and, specifically, the same monovalent hydrocarbon group as the above is illustrated. R^5 is an alkenyl group and, specifically, a vinyl group, an allyl group, a butenyl group, a pentenyl group, a hexenyl group, a heptenyl group, etc. are illustrated. n is a positive number which shows the degree of polymerization of diorganopolysiloxane, and as for n, since diorganopolysiloxane of this invention obtained is excellent in a stress release effect and compatibility to thermosetting organic resin, it is

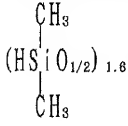
preferred that it is a positive number of the range of 1-500. As diorganopolysiloxane of such a (D) ingredient, specifically, The dimethylpolysiloxane by which chain both ends were blocked by the dimethylvinyl siloxy group, the dimethylpolysiloxane by which chain both ends were blocked by the dimethylallyl siloxy group, the dimethylpolysiloxane by which chain both ends were blocked by the dimethylhexenyl siloxy group, The methylethyl polysiloxane by which chain both ends were blocked by the dimethylvinyl siloxy group, the methylethyl polysiloxane by which chain both ends were blocked by the dimethylallyl siloxy group, the methylphenyl polysiloxane by which chain both ends were blocked by the MEJIME chill vinyl siloxy group, The methylphenyl polysiloxane by which chain both ends were blocked by the dimethylallyl siloxy group, The methylphenyl polysiloxane by which chain both ends were blocked by the dimethylhexenyl siloxy group, The methylphenyl polysiloxane by which chain both ends were blocked by the diphenylvinyl siloxy group, The dimethylsiloxane methylphenyl siloxane copolymer in which chain both ends were blocked by the dimethylvinyl siloxy group, the dimethylsiloxane diphenyl siloxane copolymer in which chain both ends were blocked by the dimethylvinyl siloxy group, Dimethylsiloxane JIFENIRUSHIRO by which chain both ends were blocked by the dimethylallyl siloxy group. The diphenylpolysiloxane etc. by which a KISAN copolymer and chain both ends were blocked by the dimethylvinyl siloxy group are illustrated.

[0019]In the manufacturing method of this invention, the addition of the (C) ingredient and the (D) ingredient requires that the number of mols of the aliphatic unsaturated bonds included in the (C) ingredient and the (D) ingredient to 1 mol of silicon atom absorbed water matter atoms in organopolysiloxane of the (B) ingredient should be the quantity which turns into more than the equivalent. The ratio of the addition of the (C) ingredient and the (D) ingredient is arbitrary, and is not limited in particular.

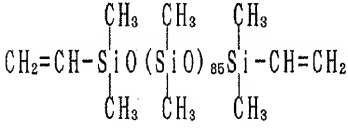
[0020]In the manufacturing method of this invention, the alkoxy silylalkene of the (E) ingredient is an ingredient for introducing an alkoxy silyl alkyl group into organopolysiloxane residue. (E) Specifically as an alkoxy silylalkene of an ingredient, trimethoxy vinylsilane, TORIETOKISHI vinylsilane, methyldi methoxy vinylsilane, allyl trimethoxysilane, allyl methyldiethoxysilane, methoxy diphenyl vinylsilane, etc. are illustrated. When the addition of the (E) ingredient is arbitrary and an alkoxy silyl alkyl group needs to be introduced into diorganopolysiloxane of this invention, it can be made to react with the (C) ingredient and the (D) ingredient in the manufacturing method of this invention. In the manufacturing method of this invention, in adding the (E) ingredient, (B) To one silicon atom absorbed water matter atom in an ingredient, if the number of the aliphatic unsaturated bonds in the (C) ingredient, the (D) ingredient, and the (E) ingredient is less than one, Diorganopolysiloxane of obtained this invention, It will have the organopolysiloxane residue which has some silicon atom absorbed water matter atoms in chain both ends, and if it is one or more pieces, it will have the organopolysiloxane residue which does not have a silicon atom absorbed water matter atom in chain both ends.

[0021]By not limiting a reaction procedure in particular, for example, mixing the (A) ingredient and the (B) ingredient first in the manufacturing method of this invention, and adding the (C) ingredient and the (D) ingredient in this system, Prepare the diorganopolysiloxane which has the organopolysiloxane residue which has a silicon atom atomic union hydrogen atom and an epoxy group content organic group to chain both ends, and it ranks second to them, The JIORUGANO polish oxane which has the organopolysiloxane residue which has an epoxy group content organic group and an alkoxy silyl alkyl group in chain both ends by adding the (E) ingredient in this system can be prepared, Prepare the organopolysiloxane which has a silicon atom absorbed water matter atom and an alkoxy silyl alkyl group by mixing the (A) ingredient and the (B) ingredient first and adding the (E) ingredient in this system, and it ranks second, By adding the (C) ingredient and the (D) ingredient in this system, the diorganopolysiloxane which has the organopolysiloxane residue which has an epoxy group content organic group and an alkoxy silyl alkyl group in chain both ends can be prepared.
[0022]In the manufacturing method of this invention, as for reaction temperature, in order not to limit the reaction temperature in particular but to complete an addition reaction promptly, it is preferred that it is the range of 50-150 **. An organic solvent can be used in the manufacturing method of this invention. Specifically as an organic solvent which can be used by this invention, ketone system organic solvents, such as aliphatic series system organic solvent; acetone, such as aromatic system organic solvent; hexane, such as toluene and xylene, heptane, and octane, and methyl ethyl ketone, etc. are illustrated. Thus, although diorganopolysiloxane of manufactured this invention is obtained as a reaction mixture, Are separable with unreacted organopolysiloxane by settling, Separation refinement of organopolysiloxane of this invention and the unreacted organopolysiloxane can be carried out using the difference of the solubility to an organic solvent, or separation refinement can be carried out by a gel permeation chromatograph.
[0023]Since diorganopolysiloxane of this invention has epoxy group content organopolysiloxane residue in chain both ends, By making it react to thermosetting organic resin, such as an epoxy resin, phenol resin, polyimide resin, polyester resin, and polyamide resin, The characteristics which are the features of diorganopolysiloxane, such as a mold-release characteristic, weatherability, and pliability, can be given to hardening organic resin after hardening, and the internal stress of hardening organic resin can be eased.
[0024]
[Example]Hereafter, an example explains this invention. Viscosity is the value measured at 25 ** among an example. Advance of the reaction was observed by the infrared spectroscopic analysis.
[0025]
[Work example 1]It is a formula to agitating equipment, a flowing-back condenser tube, and a

500 ml [with a thermometer] 4 mouth flask. : [Formula 9]



Organopolysiloxane 20.0 weight section, formula which are come out of and expressed : [Formula 10]



It came out, dimethylpolysiloxane 20.0 weight section, allyl-glycidyl-ether 31.5 weight section, and toluene 60 weight section which are expressed were taught and heated, the moisture in a system was removed as azeotrope, and it cooled under a nitrogen atmosphere. Next, after having dropped ten drops of isopropanol solutions of 2 % of the weight-chloroplatinic acid by the syringe into this system, carrying out heating stirring and heating at 80 ** for 1.5 hours, it cooled to the room temperature. Next, after adding allyl-glycidyl-ether 10 weight section which dried by the molecular sieve and heating at 110 ** again for 2 hours, at 120 **, by scale loss pressing down of 2mmHg, toluene and superfluous allyl glycidyl ether were removed, and brown transparent liquid 62.8 weight section was obtained.

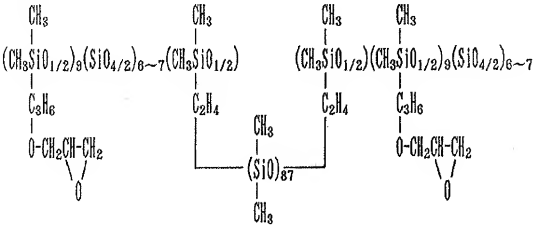
[0026]The weight per epoxy equivalent of the obtained brown transparent liquid is 390. Viscosity was 7040 centipoises.

Separation was not observed although the obtained brown transparent liquid was allowed to stand for one month at the room temperature. When the obtained brown transparent liquid was measured from infrared spectroscopic analysis, the characteristic absorption by Si-H combination was not observed. The place which analyzed the obtained brown transparent liquid by the gel permeation chromatograph, Two ingredients with the output whose degree of dispersion (Mw/Mn) the weight average molecular weight (Mw) of the output whose degree of dispersion (Mw/Mn) the weight average molecular weight (Mw) of standard polystyrene conversion is 24600, and is 1.76, and standard polystyrene conversion is 1480, and is 1.11 showed becoming. The output whose degree of dispersion (Mw/Mn) the weight average molecular weight (Mw) of standard polystyrene conversion is 24600, and is 1.76 is isolated preparatively by a gel permeation chromatograph, When the structural analysis according this

to ^{1}H-nuclear magnetic resonance analysis, ^{13}C-nuclear magnetic resonance analysis, and ^{29}Si-nuclear magnetic resonance analysis was conducted, it was checked that it is diorganopolysiloxane expressed with a lower type.

[0027]

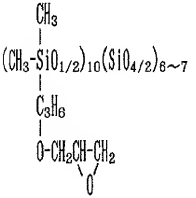
[Formula 11]



[0028]The output whose degree of dispersion (Mw/Mn) the weight average molecular weight (Mw) of standard polystyrene conversion is 1480, and is 1.11 is isolated preparatively by a gel permeation chromatograph, When the structural analysis according this to ^{1}H-nuclear magnetic resonance analysis, ^{13}C-nuclear magnetic resonance analysis, and ^{29}Si-nuclear magnetic resonance analysis was conducted, it was checked that it is organopolysiloxane expressed with a lower type.

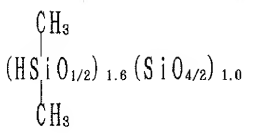
[0029]

[Formula 12]

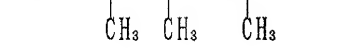


[0030]

[Work example 2]It is a formula to agitating equipment, a flowing-back condenser tube, and a 1 l. [with a thermometer] 4 mouth flask. : [Formula 13]



Organopolysiloxane 50.0 weight section, formula which are come out of and expressed :
[Formula 14]



It came out, dimethylpolysiloxane 219.2 weight section, allyl-glycidyl-ether 15.1 weight section, and toluene 270.0 weight section which are expressed were taught and heated, the moisture in a system was removed as azeotrope, and it cooled under a nitrogen atmosphere. Next, after having dropped ten drops of isopropanol solutions of 2 % of the weight-chloroplatinic acid by the syringe into this system, carrying out heating stirring and heating at 80 ** for 3 hours, it cooled to the room temperature. Next, after adding allyl-glycidyl-ether 50.0 weight section which dried by the molecular sieve and heating at 110 ** again for 2 hours, at 120 **, by scale loss pressing down of 2mmHg, toluene and superfluous allyl glycidyl ether were removed, and nebula fluid 316.6 weight section was obtained.

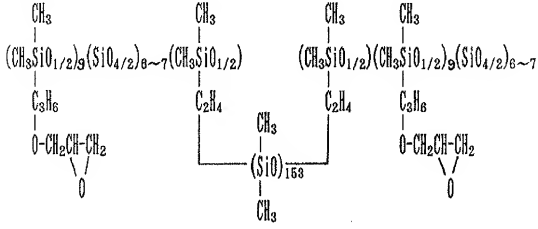
[0031]The weight per epoxy equivalent of the viscosity of the obtained nebula fluid is 879. Viscosity was 12800 centipoises.

Separation was not observed although the obtained nebula fluid was allowed to stand for four months at the room temperature. When the obtained nebula fluid was measured by the infrared spectroscopic analysis, the characteristic absorption by Si-H combination was not observed. The place which measured the obtained nebula fluid by the gel permeation chromatograph, The weight average molecular weight (Mw) of the output whose degree of dispersion (Mw/Mn) the weight average molecular weight (Mw) of standard polystyrene conversion is 53400, and is 2.44, and standard polystyrene conversion consists of two ingredients with the output whose (Mw/Mn) 1540 and a degree of dispersion is 1.12, The weight ratio was 93.2:6.7. The output whose degree of dispersion (Mw/Mn) the weight average molecular weight (Mw) of standard polystyrene conversion is 53400, and is 2.44 is isolated preparatively by a gel permeation chromatograph, When the structural analysis according this to ^{1}H-nuclear magnetic resonance analysis, ^{13}C-nuclear magnetic resonance analysis, and

^{29}Si-nuclear magnetic resonance analysis was conducted, it was checked that it is diorganopolysiloxane expressed with a lower type.

[0032]

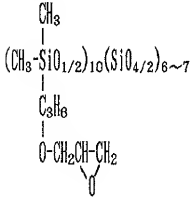
[Formula 15]



[0033]The output whose degree of dispersion (Mw/Mn) the weight average molecular weight (Mw) of standard polystyrene conversion is 1540, and is 1.12 is isolated preparatively by a gel permeation chromatograph, When the structural analysis according this to ^{1}H-nuclear magnetic resonance analysis, ^{13}C-nuclear magnetic resonance analysis, and ^{29}Si-nuclear magnetic resonance analysis was conducted, it was checked that it is organopolysiloxane expressed with a lower type.

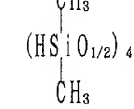
[0034]

[Formula 16]

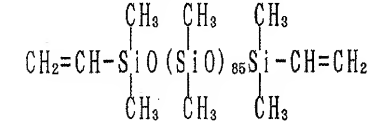


[0035]

[Work example 3]It is a formula to agitating equipment, a flowing-back condenser tube, and a 500-ml 4 mouth flask with a thermometer. : [Formula 17]



Tetrakis dimethyl siloxysilane 10 weight section, formula which are come out of and expressed : [Formula 18]

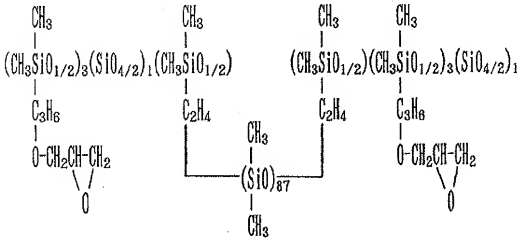


It came out, dimethylpolysiloxane 98.5 weight section, allyl-glycidyl-ether 10.4 weight section, and toluene 150 weight section which are expressed were taught and heated, the moisture in a system was removed as azeotrope, and it cooled under a nitrogen atmosphere. Next, after having dropped five drops of isopropanol solutions of 2 % of the weight-chloroplatinic acid by the syringe into this system, carrying out heating stirring and heating at 100 ** for 0.5 hour, it cooled to the room temperature. Next, after adding allyl-glycidyl-ether 10.9 weight section which dried by the molecular sieve and heating at 110 ** again for 2 hours, at 120 **, by scale loss pressing down of 2mmHg, toluene and superfluous allyl glycidyl ether were removed, and yellowish white fluid 115.5 weight section was obtained.

[0036]The viscosity of the obtained yellowish white fluid was 1340 centipoises. having allowed the obtained yellowish white fluid to stand for ten months at the room temperature -- ** -- generation of white precipitation was observed slightly. The weight per epoxy equivalent of the upper yellowish white fluid was 1300. When the upper yellowish white fluid was measured by the infrared spectroscopic analysis, the characteristic absorption by Si-H combination of output was observed slightly. When the gel permeation chromatograph analyzed the obtained yellow fluid, the weight average molecular weight (Mw) of standard polystyrene conversion was 3180, and the degree of dispersion (Mw/Mn) was 1.97. When the structural analysis according this yellowish white fluid to ^{1}H-nuclear magnetic resonance analysis, ^{13}C-nuclear magnetic resonance analysis, and ^{29}Si-nuclear magnetic resonance analysis was conducted, it was checked that it is diorganopolysiloxane expressed with a lower type.

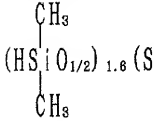
[0037]

[Formula 19]

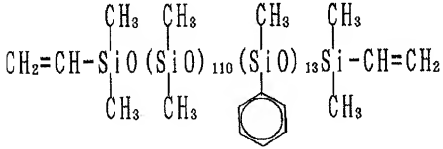


[0038]

[Work example 4]It is a formula to agitating equipment, a flowing-back condenser tube, and a 500-ml 4 mouth flask with a thermometer. : [Formula 20]



Organopolysiloxane 40 weight section, formula which are come out of and expressed : [Formula 21]



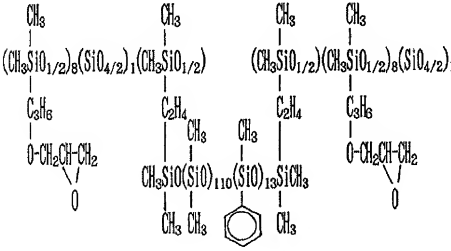
It came out, dimethylsiloxane methylphenyl siloxane copolymer 127.8 weight section, allyl-glycidyl-ether 37.0 weight section, and toluene 80 weight section which are expressed were taught and heated, the moisture in a system was removed as azeotrope, and it cooled under a nitrogen atmosphere. Next, after having dropped ten drops of isopropanol solutions of 2 % of the weight-chloroplatinic acid by the syringe into this system, carrying out heating stirring and heating at 120 ** for 1.5 hours, it cooled to the room temperature. Next, after adding allyl-glycidyl-ether 11.5 weight section which dried by the molecular sieve and heating at 120 ** again for 1 hour, at 120 **, by scale loss pressing down of 2mmHg, toluene and superfluous allyl glycidyl ether were removed, and light-brown transparent liquid 205.9 weight section was

obtained.

[0039]The viscosity of the obtained light-brown transparent liquid was 10000 centipoises. When the obtained light-brown transparent liquid was allowed to stand for four months at the room temperature, it separated into the brown transparent liquid at the upper layer, and separated into the lower layer at the brown opaque fluid, and the weight ratio was 8:1. The place which analyzed the upper light-brown transparent liquid by the gel permeation chromatograph, It consists of two ingredients with the output whose degree of dispersion (Mw/Mn) the weight average molecular weight (Mw) of the output whose degree of dispersion (Mw/Mn) the weight average molecular weight (Mw) of standard polystyrene conversion is 39500, and is 2.12, and standard polystyrene conversion is 1380, and is 1.06, The weight ratio was 95.4:4.6. The output whose degree of dispersion (Mw/Mn) the weight average molecular weight (Mw) of standard polystyrene conversion is 39500, and is 2.12 is isolated preparatively by a gel permeation chromatograph, When the structural analysis according this to ^{1}H-nuclear magnetic resonance analysis, ^{13}C-nuclear magnetic resonance analysis, and ^{29}Si-nuclear magnetic resonance analysis was conducted, it was checked that it is diorganopolysiloxane expressed with a lower type.

[0040]

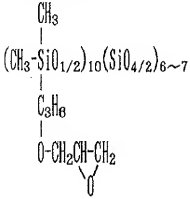
[Formula 22]



[0041]The output whose degree of dispersion (Mw/Mn) the weight average molecular weight (Mw) of standard polystyrene conversion is 1380, and is 1.06 is isolated preparatively by a gel permeation chromatograph, When the structural analysis according this to ^{1}H-nuclear magnetic resonance analysis, ^{13}C-nuclear magnetic resonance analysis, and ^{29}Si-nuclear magnetic resonance analysis was conducted, it was checked that it is organopolysiloxane expressed with a lower type.

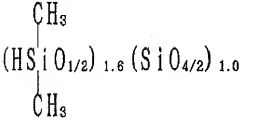
[0042]

[Formula 23]

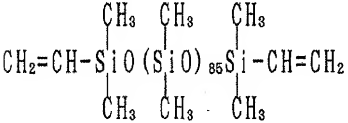


[0043]

[Work example 5]It is a formula to agitating equipment, a flowing-back condenser tube, and a 4 per l. mouth flask with a thermometer. : [Formula 24]



Organopolysiloxane 50 weight section, formula which are come out of and expressed : [Formula 25]



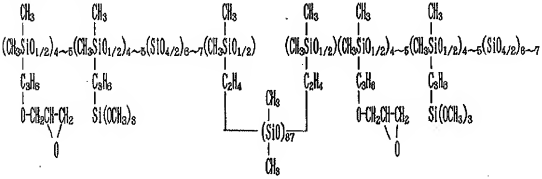
It came out, dimethylpolysiloxane 131.8 weight section expressed, allyl-glycidyl-ether 15.2 weight section, allyl trimethoxysilane 21.4 weight section, and toluene 200 weight section were taught and heated, the moisture in a system was removed as azeotrope, and it cooled under a nitrogen atmosphere. Next, ten drops of isopropanol solutions of 2 % of the weight-chloroplatinic acid were dropped by the syringe into this system, and heating stirring was carried out, and at 120 **, it heated for 1 hour and cooled to the room temperature. Next, after adding allyl-glycidyl-ether 15.1 weight section and allyl trimethoxysilane 21.4 weight section which dried by the molecular sieve and heating at 110 ** again for 2 hours, at 120 ** by scale loss pressing down of 2mmHg. Toluene and unreacted allyl glycidyl ether, and allyl trimethoxysilane were removed, and brown opaque fluid 235.4 weight section was obtained.

[0044]The obtained brown opaque fluid was brown transparence above 115 **. The viscosity of

the obtained brown opaque fluid was 2800 centipoises. When the infrared spectroscopic analysis of the obtained brown opaque fluid was conducted, the characteristic absorption by Si-H combination was observed slightly. When the obtained brown opaque fluid was allowed to stand for five months at the room temperature, it separated into the nebula fluid at the upper layer, and separated into the lower layer at the brown transparent liquid, and the weight ratio was 18:1. The place which analyzed the upper nebula fluid by the gel permeation chromatograph, It consists of two ingredients with the output whose degree of dispersion (Mw/Mn) the weight average molecular weight (Mw) of the output whose degree of dispersion (Mw/Mn) the weight average molecular weight (Mw) of standard polystyrene conversion is 30300, and is 2.21, and standard polystyrene conversion is 1910, and is 1.07, The weight ratio was 90.8:9.2. The output whose degree of dispersion (Mw/Mn) the weight average molecular weight (Mw) of standard polystyrene conversion is 30300, and is 2.21 is isolated preparatively by a gel permeation chromatograph, When the structural analysis according this to ^{1}H-nuclear magnetic resonance analysis, ^{13}C-nuclear magnetic resonance analysis, and ^{29}Si-nuclear magnetic resonance analysis was conducted, it was checked that it is diorganopolysiloxane expressed with a lower type.

[0045]

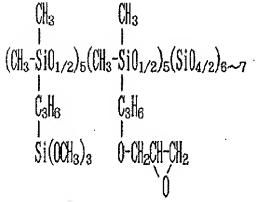
[Formula 26]



[0046]The output whose degree of dispersion (Mw/Mn) the weight average molecular weight (Mw) of standard polystyrene conversion is 1910, and is 1.07 is isolated preparatively by a gel permeation chromatograph, When the structural analysis according this to ^{1}H-nuclear magnetic resonance analysis, ^{13}C-nuclear magnetic resonance analysis, and ^{29}Si-nuclear magnetic resonance analysis was conducted, it was checked that it is organopolysiloxane expressed with a lower type.

[0047]

[Formula 27]



[0048]

[Effect of the Invention]Diorganopolysiloxane of this invention is new diorganopolysiloxane which has epoxy group content organopolysiloxane residue in chain both ends.

The manufacturing method of this invention has the feature that such new diorganopolysiloxane can be manufactured.

[Translation done.]

TECHNICAL FIELD

[Industrial Application]This invention relates to new diorganopolysiloxane and a manufacturing method for the same which have epoxy group content organopolysiloxane residue in chain both ends in detail about diorganopolysiloxane and a manufacturing method for the same.

[Translation done.]

PRIOR ART

[Description of the Prior Art]The diorganopolysiloxane which has an epoxy group, By blending with thermosetting organic resin, such as an epoxy resin and phenol resin, the characteristics which are the features of diorganopolysiloxane, such as a mold-release characteristic, weatherability, and pliability, can be given to hardening organic resin after hardening, and the internal stress of this hardening organic resin can be eased further.
[0003]As diorganopolysiloxane which has such an epoxy group, For example, the diorganopolysiloxane (refer to JP,2-69528,A) which has an epoxy group in diorganopolysiloxane (refer to JP,61-60726,A) or chain both ends which has an epoxy group in a chain side chain is proposed.

[Translation done.]

EFFECT OF THE INVENTION

[Effect of the Invention]Diorganopolysiloxane of this invention is new diorganopolysiloxane which has epoxy group content organopolysiloxane residue in chain both ends.
The manufacturing method of this invention has the feature that such new diorganopolysiloxane can be manufactured.

[Translation done.]

TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention]However, the diorganopolysiloxane proposed by JP,61-60726,A, When the reactivity of the epoxy group which it has in the chain side chain is low and this is blended with thermosetting organic resin, such as an epoxy resin and phenol resin, by the unreacted epoxy group in diorganopolysiloxane. The diorganopolysiloxane which there is a problem that the physical property of the obtained hardening organic resin changes temporally, and was proposed by JP,2-69528,A had the problem that the epoxy group in a monad was limited to two pieces.

[0005]this invention person reached this invention, as a result of trying hard wholeheartedly, in order to solve the above-mentioned problem.

[0006]That is, the purpose of this invention is to provide new diorganopolysiloxane and a manufacturing method for the same which have epoxy group content organopolysiloxane residue in chain both ends.

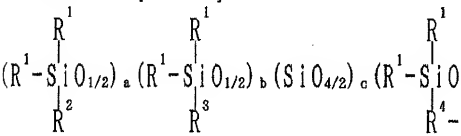
[Translation done.]

* NOTICES *

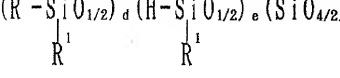
1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

OPERATION

[The means for solving a problem, and its operation] This invention is a general formula to chain both ends. : [Formula 3]



{R^1 is a monovalent hydrocarbon group except an alkenyl group among a formula, and R^2 is the monovalent hydrocarbon group or hydrogen atom except an alkenyl group, R^3 An epoxy group content organic group or an alkoxy silyl alkyl group, However, at least one in R^3 is an epoxy group content organic group, R^4 is a bivalence hydrocarbon group, and a is 0 or a positive number, b is a positive number, and c is a positive number, and a/c is a positive number of 0-4, b/c is a positive number of 0.05-4, and (a+b)/c is a positive number of 0.2-4. The bottom of existence of the diorganopolysiloxane which has the epoxy group content organopolysiloxane residue expressed with}, and (A) platinum system catalyst, (B) general formula : [Formula 4]

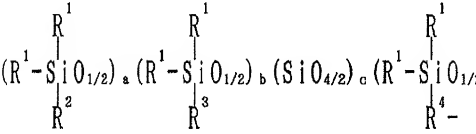


{R^1 is a monovalent hydrocarbon group except an alkenyl group among a formula, and d is 0 or a positive number, e is a positive number, and f is a positive number, and d/f is a positive number of 0-4, e/f is a positive number of 0.05-4, and (d+e)/f is a positive number of 0.2-4. The organopolysiloxane expressed with}, the organic compound which has the (C) epoxy group and aliphatic unsaturated bonds, (D) The addition of the diorganopolysiloxane which has an alkenyl group in chain both ends, and {ingredient and (D) ingredient is a quantity from which the number of mols of the aliphatic unsaturated bonds included in the (C) ingredient and the (D) ingredient to 1 mol of silicon atom absorbed water matter atoms in the (B) ingredient becomes more than the equivalent. [(C)] It is related with the manufacturing method of the diorganopolysiloxane carrying out the addition reaction of the alkoxy silylalkene of} and the (E) arbitrary dose.

[0008]First, diorganopolysiloxane of this invention is explained in detail.

[0009]Diorganopolysiloxane of this invention is a general formula to chain both ends. :

[Formula 5]

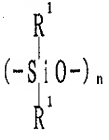


It comes out and has the epoxy group content organopolysiloxane residue expressed. R^1 is a monovalent hydrocarbon group except an alkenyl group among an upper type, and specifically, Aryl groups, such as cycloalkyl group; phenyl groups, such as alkyl group; cyclopentylic groups, such as a methyl group, an ethyl group, a propyl group, a butyl group, a pentyl group, and a hexyl group, a cyclohexyl group, and a cycloheptyl group, a tolyl group, and a xylyl group; Benzyl, a phenethyl group, Aralkyl groups, such as a phenylpropyl group; monovalent hydrocarbon groups, such as substituted alkyl groups, such as a chloromethyl group and a 3,3,3-trifluoropropyl group, are illustrated. R^2 is a monovalent hydrocarbon group or a hydrogen atom except an alkenyl group, and, specifically, the same monovalent hydrocarbon group as the above is illustrated as a monovalent hydrocarbon group of R^2. R^3 is an epoxy group content organic group or an alkoxy silyl alkyl group, however at least one in R^3 is an epoxy group content organic group. As an epoxy group content organic group of R^3, specifically, Epoxy group content organic groups, such as a glycidoxy ethyl group, a glycidoxy propyl group, and a 3,4-epoxycyclohexyl ethyl group, are illustrated, and as an alkoxy silyl alkyl group of R^3, Specifically, alkoxy silyl alkyl groups, such as a trimethoxysilyl ethyl group, a

trimethoxysilylpropyl group, a dimethoxymethyl silylpropyl group, a methoxy dimethylsilyl propyl group, a triethoxy silyl ethyl group, and a tripropoxy silylpropyl group, are illustrated. R^4 is a bivalence hydrocarbon group and, specifically, a methylmethylene group, ethylene, a methyl ethylene group, a propylene group, a butylene group, a pentylene group, etc. are illustrated. Diorganopolysiloxane of this invention is combined with the above-mentioned epoxy group content organopolysiloxane residue via an R^4 group.

[0010]a is 0 or a positive number which shows the number of monofunctional siloxane units (M unit) which have a monovalent hydrocarbon group or a silicon atom absorbed water matter atom except an alkenyl group among an upper type, b is a positive number which shows the number of monofunctional siloxane units (M unit) which have an epoxy group content organic group or an alkoxy silyl alkyl group, c is a positive number which shows the number of tetrafunctional siloxane units (Q unit), each ratio and a/c are the positive numbers of 0-4, and b/c is a positive number of 0.05-4, and (a+b)/c is a positive number of 0.2-4. Monofunctional siloxane units (M unit) cannot have this [good] for four pieces to one tetrafunctional siloxane units (Q unit), and diorganopolysiloxane of this invention receives thermosetting organic resin, it is because monofunctional siloxane units (M unit) which have an epoxy group content organic group or an alkoxy silyl alkyl group need to be at least 0.05 piece in order to excel in a stress release effect and compatibility.

[0011]Although diorganopolysiloxane of this invention has epoxy group content organopolysiloxane residue in chain both ends, diorganopolysiloxane in particular of a principal chain part is not limited, for example, it is a general formula. : [Formula 6]

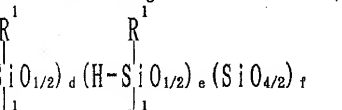


It comes out and the diorganopolysiloxane expressed is mentioned. R^1 is a monovalent hydrocarbon group except an alkenyl group among an upper type, and, specifically, said same monovalent hydrocarbon group is illustrated. As for n, although n is a positive number which shows the degree of polymerization of diorganopolysiloxane which is a main chain among an upper type and it is not limited in particular, in order for diorganopolysiloxane of this invention to be excellent in a stress release effect and compatibility to thermosetting organic resin, it is preferred that it is the range of 1-500. As diorganopolysiloxane of such a principal chain part, specifically, Dimethylpolysiloxane, a methylethyl polysiloxane, Diorganopolysiloxane, such as a methylphenyl polysiloxane, a dimethylsiloxane methylphenyl siloxane copolymer, a

dimethylsiloxane diphenyl siloxane copolymer, and a diphenylpolysiloxane, is illustrated.
[0012]At a room temperature, diorganopolysiloxane of this invention is liquefied or a solid state.
Although the molecular weight in particular is not limited, when this is blended with thermosetting organic resin, such as an epoxy resin and phenol resin, since compatibility with this organic resin is good, it is preferred [the molecular weight of diorganopolysiloxane of this invention] that it is the range of 500-1,000,000.

[0013]Below, a manufacturing method of diorganopolysiloxane of this invention is explained.
[0014]In a manufacturing method of this invention, a platinum system catalyst of the (A) ingredient is a catalyst for carrying out the addition reaction of the aliphatic unsaturated bonds in a silicon atom absorbed water matter atom in the (B) ingredient, the (C) ingredient, the (D) ingredient, and the (E) ingredient. (A) A platinum system catalyst of an ingredient will not usually be limited, especially if used as a hydrosilylation addition reaction catalyst. Specifically as a platinum system catalyst of such a (A) ingredient, activated carbon of an alcohol solution of chloroplatinic acid and chloroplatinic acid, a complex of platinum and unsaturation aliphatic hydrocarbon, a complex of platinum and a vinyl siloxane, platinum black, and platinum support, etc. are illustrated. In a manufacturing method of this invention, an addition in particular of the (A) ingredient is not limited, but is the usual catalyst amount, and, specifically, it is preferred that it is the range of 0.01-500 ppm as platinum metal in the (A) ingredient to the (B) ingredient.

[0015]It is an ingredient for introducing organopolysiloxane residue which combines organopolysiloxane of the (B) ingredient with chain both ends of diorganopolysiloxane of this invention in a manufacturing method of this invention, and is a general formula. : [Formula 7]



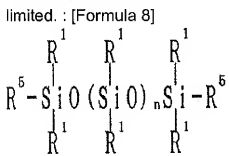
It is come out and expressed. R^1 is a monovalent hydrocarbon group except an alkenyl group among an upper type, and specifically, Aryl groups, such as cycloalkyl group; phenyl groups, such as alkyl group; cyclopentylic groups, such as a methyl group, an ethyl group, a propyl group, a butyl group, a pentyl group, and a hexyl group, a cyclohexyl group, and a cycloheptyl group, a tolyl group, and a xylyl group; Benzyl, a phenethyl group, Aralkyl groups, such as a phenylpropyl group; monovalent hydrocarbon groups, such as substituted alkyl groups, such

as a chloromethyl group and a 3,3,3-trifluoropropyl group, are illustrated. d is 0 or the positive number which shows the number of the monofunctional siloxane units (M unit) which have a monovalent hydrocarbon group except an alkenyl group, e is a positive number which shows the number of the monofunctional siloxane units (M unit) which have a silicon atom absorbed water matter atom, f is a positive number which shows the number of tetrafunctional siloxane units (Q unit), each ratio and d/f are the positive numbers of 0-4, and e/f is a positive number of 0.05-4, and (d+e)/f is a positive number of 0.2-4. This cannot have eight M of monofunctional siloxane-units unit [good] for four pieces to one tetrafunctional siloxane units (Q unit), it is because the monofunctional siloxane units (M unit) which have a silicon atom absorbed water matter atom need to be at least 0.05 piece in order for diorganopolysiloxane of this invention to have reactivity to thermosetting organic resin and to be excellent in compatibility.

[0016]Such organopolysiloxane of the (B) ingredient can be conventionally manufactured by the well-known method. (B) How to specifically carry out the cohydrolysis of a tetra halo silane and the mono- halo silane as a manufacturing method of an ingredient, The method of carrying out the cohydrolysis of tetra alkoxysilane and the mono- alkoxysilane, the method of hydrolyzing and re-equilibration polymerizing tetra alkoxysilane and tetra ORGANO disiloxane, etc. are illustrated, and preferably in a hydrochloric acid aqueous solution, It is the method (refer to JP,61-195129,A) of trickling tetra alkoxysilane, stirring the organic silicon compound chosen from the group which consists of hexa ORGANO disiloxane, tetra ORGANO disiloxane, a trio luganot halo silane, and a JIORUGANO halo silane.

[0017]In the manufacturing method of this invention, the organic compound which has the epoxy group and aliphatic unsaturated bonds of the (C) ingredient is an ingredient for introducing an epoxy group content organic group into organopolysiloxane residue. (C) As an organic compound which it has, the epoxy group and aliphatic unsaturated bonds of an ingredient specifically, Vinyl glycidoxy ether, allyl glycidoxy ether, Butenyl glycidoxy ether, 1,2-epoxy-4-vinylcyclohexane, 2,3-epoxy-5-vinyl norbornene, 1,2-epoxy-1-methyl-4-isopropenylcyclohexane, etc. are illustrated.

[0018]In a manufacturing method of this invention, diorganopolysiloxane of the (D) ingredient is an ingredient which forms a main chain of diorganopolysiloxane of this invention. Specifically, especially diorganopolysiloxane of such a (D) ingredient is a general formula, although not limited. : [Formula 8]



(R^1 is a monovalent hydrocarbon group except an alkenyl group among a formula, R^5 is an alkenyl group, and n is a positive number.) -- it is expressed. R^1 is a monovalent hydrocarbon group except an alkenyl group among an upper type, and, specifically, the same monovalent hydrocarbon group as the above is illustrated. R^5 is an alkenyl group and, specifically, a vinyl group, an allyl group, a butenyl group, a pentenyl group, a hexenyl group, a heptenyl group, etc. are illustrated. n is a positive number which shows the degree of polymerization of diorganopolysiloxane, and as for n, since diorganopolysiloxane of this invention obtained is excellent in a stress release effect and compatibility to thermosetting organic resin, it is preferred that it is a positive number of the range of 1-500. As diorganopolysiloxane of such a (D) ingredient, specifically, The dimethylpolysiloxane by which chain both ends were blocked by the dimethylvinyl siloxy group, the dimethylpolysiloxane by which chain both ends were blocked by the dimethylallyl siloxy group, the dimethylpolysiloxane by which chain both ends were blocked by the dimethylhexenyl siloxy group, The methylethyl polysiloxane by which chain both ends were blocked by the dimethylvinyl siloxy group, the methylethyl polysiloxane by which chain both ends were blocked by the dimethylallyl siloxy group, the methylphenyl polysiloxane by which chain both ends were blocked by the MEJIME chill vinyl siloxy group, The methylphenyl polysiloxane by which chain both ends were blocked by the dimethylallyl siloxy group, The methylphenyl polysiloxane by which chain both ends were blocked by the dimethylhexenyl siloxy group, The methylphenyl polysiloxane by which chain both ends were blocked by the diphenylvinyl siloxy group, The dimethylsiloxane methylphenyl siloxane copolymer in which chain both ends were blocked by the dimethylvinyl siloxy group, the dimethylsiloxane diphenyl siloxane copolymer in which chain both ends were blocked by the dimethylvinyl siloxy group, Dimethylsiloxane JIFENIRUSHIRO by which chain both ends were blocked by the dimethylallyl siloxy group. The diphenylpolysiloxane etc. by which a KISAN copolymer and chain both ends were blocked by the dimethylvinyl siloxy group are illustrated.

[0019]In the manufacturing method of this invention, the addition of the (C) ingredient and the (D) ingredient requires that the number of mols of the aliphatic unsaturated bonds included in the (C) ingredient and the (D) ingredient to 1 mol of silicon atom absorbed water matter atoms in organopolysiloxane of the (B) ingredient should be the quantity which turns into more than the equivalent. The ratio of the addition of the (C) ingredient and the (D) ingredient is arbitrary, and is not limited in particular.

[0020]In the manufacturing method of this invention, the alkoxy silylalkene of the (E) ingredient is an ingredient for introducing an alkoxy silyl alkyl group into organopolysiloxane residue. (E) Specifically as an alkoxy silylalkene of an ingredient, trimethoxy vinylsilane, TORIETOKISHI vinylsilane, methyldi methoxy vinylsilane, allyl trimethoxysilane, allyl methyldiethoxysilane, methoxy diphenyl vinylsilane, etc. are illustrated. When the addition of the (E) ingredient is

arbitrary and an alkoxy silyl alkyl group needs to be introduced into diorganopolysiloxane of this invention, it can be made to react with the (C) ingredient and the (D) ingredient in the manufacturing method of this invention. In the manufacturing method of this invention, in adding the (E) ingredient, (B) To one silicon atom absorbed water matter atom in an ingredient, if the number of the aliphatic unsaturated bonds in the (C) ingredient, the (D) ingredient, and the (E) ingredient is less than one, Diorganopolysiloxane of obtained this invention, It will have the organopolysiloxane residue which has some silicon atom absorbed water matter atoms in chain both ends, and if it is one or more pieces, it will have the organopolysiloxane residue which does not have a silicon atom absorbed water matter atom in chain both ends.

[0021]By not limiting a reaction procedure in particular, for example, mixing the (A) ingredient and the (B) ingredient first in the manufacturing method of this invention, and adding the (C) ingredient and the (D) ingredient in this system, Prepare the diorganopolysiloxane which has the organopolysiloxane residue which has a silicon atom atomic union hydrogen atom and an epoxy group content organic group to chain both ends, and it ranks second to them, The JIORUGANO polish oxane which has the organopolysiloxane residue which has an epoxy group content organic group and an alkoxy silyl alkyl group in chain both ends by adding the (E) ingredient in this system can be prepared, Prepare the organopolysiloxane which has a silicon atom absorbed water matter atom and an alkoxy silyl alkyl group by mixing the (A) ingredient and the (B) ingredient first and adding the (E) ingredient in this system, and it ranks second, By adding the (C) ingredient and the (D) ingredient in this system, the diorganopolysiloxane which has the organopolysiloxane residue which has an epoxy group content organic group and an alkoxy silyl alkyl group in chain both ends can be prepared.

[0022]In the manufacturing method of this invention, as for reaction temperature, in order not to limit the reaction temperature in particular but to complete an addition reaction promptly, it is preferred that it is the range of 50-150 **. An organic solvent can be used in the manufacturing method of this invention. Specifically as an organic solvent which can be used by this invention, ketone system organic solvents, such as aliphatic series system organic solvent; acetone, such as aromatic system organic solvent; hexane, such as toluene and xylene, heptane, and octane, and methyl ethyl ketone, etc. are illustrated. Thus, although diorganopolysiloxane of manufactured this invention is obtained as a reaction mixture, Are separable with unreacted organopolysiloxane by settling, Separation refinement of organopolysiloxane of this invention and the unreacted organopolysiloxane can be carried out using the difference of the solubility to an organic solvent, or separation refinement can be carried out by a gel permeation chromatograph.

[0023]Since diorganopolysiloxane of this invention has epoxy group content organopolysiloxane residue in chain both ends, By making it react to thermosetting organic resin, such as an epoxy resin, phenol resin, polyimide resin, polyester resin, and polyamide

resin, The characteristics which are the features of diorganopolysiloxane, such as a mold-release characteristic, weatherability, and pliability, can be given to hardening organic resin after hardening, and the internal stress of hardening organic resin can be eased.

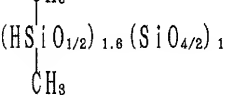
[Translation done.]

EXAMPLE

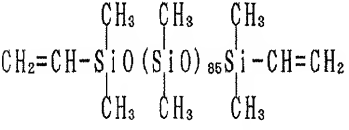
[Example]Hereafter, an example explains this invention. Viscosity is the value measured at 25 ** among an example. Advance of the reaction was observed by the infrared spectroscopic analysis.

[0025]

[Work example 1]It is a formula to agitating equipment, a flowing-back condenser tube, and a 500 ml [with a thermometer] 4 mouth flask. : [Formula 9]



Organopolysiloxane 20.0 weight section, formula which are come out of and expressed : [Formula 10]



It came out, dimethylpolysiloxane 20.0 weight section, allyl-glycidyl-ether 31.5 weight section, and toluene 60 weight section which are expressed were taught and heated, the moisture in a system was removed as azeotrope, and it cooled under a nitrogen atmosphere. Next, after having dropped ten drops of isopropanol solutions of 2 % of the weight-chloroplatinic acid by the syringe into this system, carrying out heating stirring and heating at 80 ** for 1.5 hours, it cooled to the room temperature. Next, after adding allyl-glycidyl-ether 10 weight section which

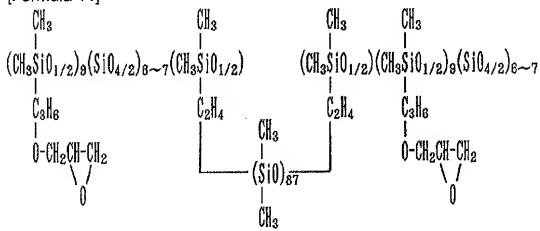
dried by the molecular sieve and heating at 110 ** again for 2 hours, at 120 **, by scale loss pressing down of 2mmHg, toluene and superfluous allyl glycidyl ether were removed, and brown transparent liquid 62.8 weight section was obtained.

[0026]The weight per epoxy equivalent of the obtained brown transparent liquid is 390. Viscosity was 7040 centipoises.

Separation was not observed although the obtained brown transparent liquid was allowed to stand for one month at the room temperature. When the obtained brown transparent liquid was measured from infrared spectroscopic analysis, the characteristic absorption by Si-H combination was not observed. The place which analyzed the obtained brown transparent liquid by the gel permeation chromatograph, Two ingredients with the output whose degree of dispersion (Mw/Mn) the weight average molecular weight (Mw) of the output whose degree of dispersion (Mw/Mn) the weight average molecular weight (Mw) of standard polystyrene conversion is 24600, and is 1.76, and standard polystyrene conversion is 1480, and is 1.11 showed becoming. The output whose degree of dispersion (Mw/Mn) the weight average molecular weight (Mw) of standard polystyrene conversion is 24600, and is 1.76 is isolated preparatively by a gel permeation chromatograph, When the structural analysis according this to ^{1}H-nuclear magnetic resonance analysis, ^{13}C-nuclear magnetic resonance analysis, and ^{29}Si-nuclear magnetic resonance analysis was conducted, it was checked that it is diorganopolysiloxane expressed with a lower type.

[0027]

[Formula 11]

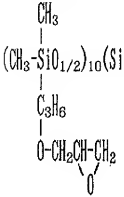


[0028]The output whose degree of dispersion (Mw/Mn) the weight average molecular weight (Mw) of standard polystyrene conversion is 1480, and is 1.11 is isolated preparatively by a gel permeation chromatograph, When the structural analysis according this to ^{1}H-nuclear magnetic resonance analysis, ^{13}C-nuclear magnetic resonance analysis, and ^{29}Si-nuclear magnetic resonance analysis was conducted, it was checked that it is organopolysiloxane

expressed with a lower type.

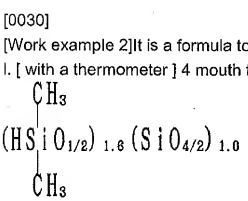
[0029]

[Formula 12]

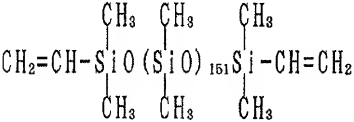


[0030]

[Work example 2]It is a formula to agitating equipment, a flowing-back condenser tube, and a 1 l. [with a thermometer] 4 mouth flask. : [Formula 13]



Organopolysiloxane 50.0 weight section, formula which are come out of and expressed : [Formula 14]



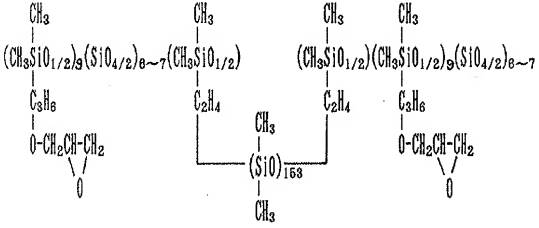
It came out, dimethylpolysiloxane 219.2 weight section, allyl-glycidyl-ether 15.1 weight section, and toluene 270.0 weight section which are expressed were taught and heated, the moisture in a system was removed as azeotrope, and it cooled under a nitrogen atmosphere. Next, after having dropped ten drops of isopropanol solutions of 2 % of the weight-chloroplatinic acid by the syringe into this system, carrying out heating stirring and heating at 80 ** for 3 hours, it cooled to the room temperature. Next, after adding allyl-glycidyl-ether 50.0 weight section which dried by the molecular sieve and heating at 110 ** again for 2 hours, at 120 **, by scale loss pressing down of 2mmHg, toluene and superfluous allyl glycidyl ether were removed, and nebula fluid 316.6 weight section was obtained.

[0031]The weight per epoxy equivalent of the viscosity of the obtained nebula fluid is 879. Viscosity was 12800 centipoises.

Separation was not observed although the obtained nebula fluid was allowed to stand for four months at the room temperature. When the obtained nebula fluid was measured by the infrared spectroscopic analysis, the characteristic absorption by Si-H combination was not observed. The place which measured the obtained nebula fluid by the gel permeation chromatograph, The weight average molecular weight (Mw) of the output whose degree of dispersion (Mw/Mn) the weight average molecular weight (Mw) of standard polystyrene conversion is 53400, and is 2.44, and standard polystyrene conversion consists of two ingredients with the output whose (Mw/Mn) 1540 and a degree of dispersion is 1.12, The weight ratio was 93.2:6.7. The output whose degree of dispersion (Mw/Mn) the weight average molecular weight (Mw) of standard polystyrene conversion is 53400, and is 2.44 is isolated preparatively by a gel permeation chromatograph, When the structural analysis according this to ^{1}H-nuclear magnetic resonance analysis, ^{13}C-nuclear magnetic resonance analysis, and ^{29}Si-nuclear magnetic resonance analysis was conducted, it was checked that it is diorganopolysiloxane expressed with a lower type.

[0032]

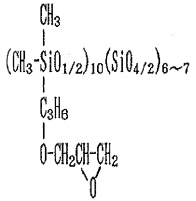
[Formula 15]



[0033]The output whose degree of dispersion (Mw/Mn) the weight average molecular weight (Mw) of standard polystyrene conversion is 1540, and is 1.12 is isolated preparatively by a gel permeation chromatograph, When the structural analysis according this to ^{1}H-nuclear magnetic resonance analysis, ^{13}C-nuclear magnetic resonance analysis, and ^{29}Si-nuclear magnetic resonance analysis was conducted, it was checked that it is organopolysiloxane expressed with a lower type.

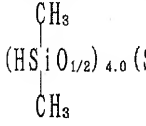
[0034]

[Formula 16]

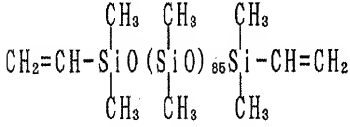


[0035]

[Work example 3]It is a formula to agitating equipment, a flowing-back condenser tube, and a 500-ml 4 mouth flask with a thermometer. : [Formula 17]



Tetrakis dimethyl siloxysilane 10 weight section, formula which are come out of and expressed : [Formula 18]



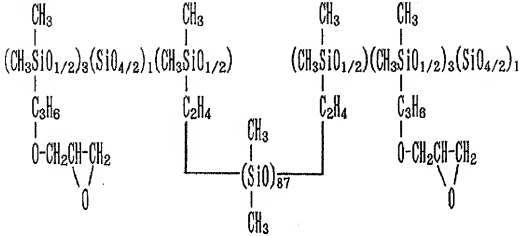
It came out, dimethylpolysiloxane 98.5 weight section, allyl-glycidyl-ether 10.4 weight section, and toluene 150 weight section which are expressed were taught and heated, the moisture in a system was removed as azeotrope, and it cooled under a nitrogen atmosphere. Next, after having dropped five drops of isopropanol solutions of 2 % of the weight-chloroplatinic acid by the syringe into this system, carrying out heating stirring and heating at 100 ** for 0.5 hour, it cooled to the room temperature. Next, after adding allyl-glycidyl-ether 10.9 weight section which dried by the molecular sieve and heating at 110 ** again for 2 hours, at 120 **, by scale loss pressing down of 2mmHg, toluene and superfluous allyl glycidyl ether were removed, and yellowish white fluid 115.5 weight section was obtained.

[0036]The viscosity of the obtained yellowish white fluid was 1340 centipoises. having allowed the obtained yellowish white fluid to stand for ten months at the room temperature -- ** -- generation of white precipitation was observed slightly. The weight per epoxy equivalent of the

upper yellowish white fluid was 1300. When the upper yellowish white fluid was measured by the infrared spectroscopic analysis, the characteristic absorption by Si-H combination of output was observed slightly. When the gel permeation chromatograph analyzed the obtained yellow fluid, the weight average molecular weight (Mw) of standard polystyrene conversion was 3180, and the degree of dispersion (Mw/Mn) was 1.97. When the structural analysis according this yellowish white fluid to ^{1}H-nuclear magnetic resonance analysis, ^{13}C-nuclear magnetic resonance analysis, and ^{29}Si-nuclear magnetic resonance analysis was conducted, it was checked that it is diorganopolysiloxane expressed with a lower type.

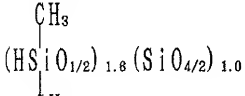
[0037]

[Formula 19]



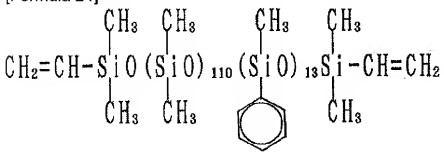
[0038]

[Work example 4]It is a formula to agitating equipment, a flowing-back condenser tube, and a 500-ml 4 mouth flask with a thermometer. : [Formula 20]



Organopolysiloxane 40 weight section, formula which are come out of and expressed :

[Formula 21]

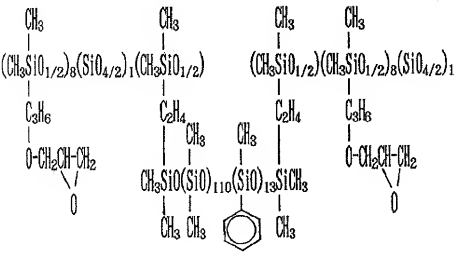


It came out, dimethylsiloxane methylphenyl siloxane copolymer 127.8 weight section, allyl-glycidyl-ether 37.0 weight section, and toluene 80 weight section which are expressed were taught and heated, the moisture in a system was removed as azeotrope, and it cooled under a nitrogen atmosphere. Next, after having dropped ten drops of isopropanol solutions of 2 % of the weight-chloroplatinic acid by the syringe into this system, carrying out heating stirring and heating at 120 ** for 1.5 hours, it cooled to the room temperature. Next, after adding allyl-glycidyl-ether 11.5 weight section which dried by the molecular sieve and heating at 120 ** again for 1 hour, at 120 **, by scale loss pressing down of 2mmHg, toluene and superfluous allyl glycidyl ether were removed, and light-brown transparent liquid 205.9 weight section was obtained.

[0039]The viscosity of the obtained light-brown transparent liquid was 10000 centipoises. When the obtained light-brown transparent liquid was allowed to stand for four months at the room temperature, it separated into the brown transparent liquid at the upper layer, and separated into the lower layer at the brown opaque fluid, and the weight ratio was 8:1. The place which analyzed the upper light-brown transparent liquid by the gel permeation chromatograph, It consists of two ingredients with the output whose degree of dispersion (Mw/Mn) the weight average molecular weight (Mw) of the output whose degree of dispersion (Mw/Mn) the weight average molecular weight (Mw) of standard polystyrene conversion is 39500, and is 2.12, and standard polystyrene conversion is 1380, and is 1.06, The weight ratio was 95.4:4.6. The output whose degree of dispersion (Mw/Mn) the weight average molecular weight (Mw) of standard polystyrene conversion is 39500, and is 2.12 is isolated preparatively by a gel permeation chromatograph, When the structural analysis according this to ^{1}H-nuclear magnetic resonance analysis, ^{13}C-nuclear magnetic resonance analysis, and ^{29}Si-nuclear magnetic resonance analysis was conducted, it was checked that it is diorganopolysiloxane expressed with a lower type.

[0040]

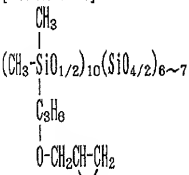
[Formula 22]



[0041]The output whose degree of dispersion (Mw/Mn) the weight average molecular weight (Mw) of standard polystyrene conversion is 1380, and is 1.06 is isolated preparatively by a gel permeation chromatograph, When the structural analysis according this to ^{1}H-nuclear magnetic resonance analysis, ^{13}C-nuclear magnetic resonance analysis, and ^{29}Si-nuclear magnetic resonance analysis was conducted, it was checked that it is organopolysiloxane expressed with a lower type.

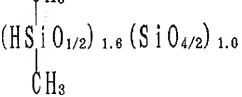
[0042]

[Formula 23]

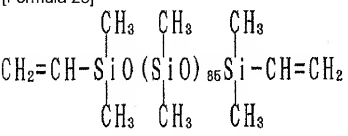


[0043]

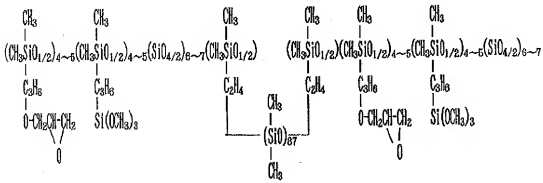
[Work example 5]It is a formula to agitating equipment, a flowing-back condenser tube, and a 4 per l. mouth flask with a thermometer. : [Formula 24]



Organopolysiloxane 50 weight section, formula which are come out of and expressed :
[Formula 25]



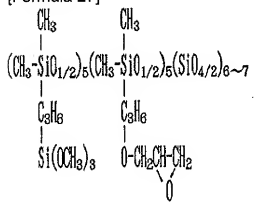
It came out, dimethylpolysiloxane 131.8 weight section expressed, allyl-glycidyl-ether 15.2 weight section, allyl trimethoxysilane 21.4 weight section, and toluene 200 weight section were taught and heated, the moisture in a system was removed as azeotrope, and it cooled under a nitrogen atmosphere. Next, ten drops of isopropanol solutions of 2 % of the weight-chloroplatinic acid were dropped by the syringe into this system, and heating stirring was carried out, and at 120 **, it heated for 1 hour and cooled to the room temperature. Next, after adding allyl-glycidyl-ether 15.1 weight section and allyl trimethoxysilane 21.4 weight section which dried by the molecular sieve and heating at 110 ** again for 2 hours, at 120 ** by scale loss pressing down of 2mmHg. Toluene and unreacted allyl glycidyl ether, and allyl trimethoxysilane were removed, and brown opaque fluid 235.4 weight section was obtained.
[0044]The obtained brown opaque fluid was brown transparence above 115 **. The viscosity of the obtained brown opaque fluid was 2800 centipoises. When the infrared spectroscopic analysis of the obtained brown opaque fluid was conducted, the characteristic absorption by Si-H combination was observed slightly. When the obtained brown opaque fluid was allowed to stand for five months at the room temperature, it separated into the nebula fluid at the upper layer, and separated into the lower layer at the brown transparent liquid, and the weight ratio was 18:1. The place which analyzed the upper nebula fluid by the gel permeation chromatograph, It consists of two ingredients with the output whose degree of dispersion (Mw/Mn) the weight average molecular weight (Mw) of the output whose degree of dispersion (Mw/Mn) the weight average molecular weight (Mw) of standard polystyrene conversion is 30300, and is 2.21, and standard polystyrene conversion is 1910, and is 1.07, The weight ratio was 90.8:9.2. The output whose degree of dispersion (Mw/Mn) the weight average molecular weight (Mw) of standard polystyrene conversion is 30300, and is 2.21 is isolated preparatively by a gel permeation chromatograph, When the structural analysis according this to ^{1}H-nuclear magnetic resonance analysis, ^{13}C-nuclear magnetic resonance analysis, and ^{29}Si-nuclear magnetic resonance analysis was conducted, it was checked that it is diorganopolysiloxane expressed with a lower type.
[0045]
[Formula 26]



[0046]The output whose degree of dispersion (Mw/Mn) the weight average molecular weight (Mw) of standard polystyrene conversion is 1910, and is 1.07 is isolated preparatively by a gel permeation chromatograph, When the structural analysis according this to ^{1}H-nuclear magnetic resonance analysis, ^{13}C-nuclear magnetic resonance analysis, and ^{29}Si-nuclear magnetic resonance analysis was conducted, it was checked that it is organopolysiloxane expressed with a lower type.

[0047]

[Formula 27]



[0048]

[Translation done.]

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1]It is an infrared spectroscopic-analysis chart of the diorganopolysiloxane prepared in Example 1.
[Drawing 2]It is a gel permeation chromatograph chart of the diorganopolysiloxane prepared in Example 1. A dotted line shows dimethylpolysiloxane of a raw material and a solid line shows the obtained brown transparent liquid.
[Drawing 3]It is an infrared spectroscopic-analysis chart of the diorganopolysiloxane prepared in Example 2.
[Drawing 4]It is a gel permeation chromatograph chart of the diorganopolysiloxane prepared in Example 2. A dotted line shows dimethylpolysiloxane of a raw material and a solid line shows the obtained nebula fluid.
[Drawing 5]It is an infrared spectroscopic-analysis chart of the diorganopolysiloxane prepared in Example 3.
[Drawing 6]It is a gel permeation chromatograph chart of the diorganopolysiloxane prepared in Example 3. A dotted line shows dimethylpolysiloxane of a raw material and a solid line shows a yellowish white fluid.
[Drawing 7]It is an infrared spectroscopic-analysis chart of the diorganopolysiloxane prepared in Example 4.
[Drawing 8]It is a gel permeation chromatograph chart of the diorganopolysiloxane prepared in Example 4. A dotted line shows the dimethylsiloxane methylphenyl siloxane copolymer of a raw material, and a solid line shows the obtained light-brown transparent liquid.
[Drawing 9]It is an infrared spectroscopic-analysis chart of the diorganopolysiloxane prepared in Example 5.
[Drawing 10]It is a gel permeation chromatograph chart of the diorganopolysiloxane prepared in Example 5. A dotted line shows dimethylpolysiloxane of a raw material and a solid line

shows the obtained brown opaque fluid.

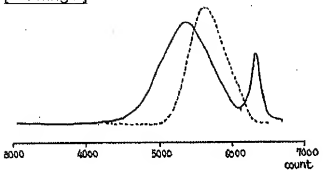
[Translation done.]

* NOTICES *

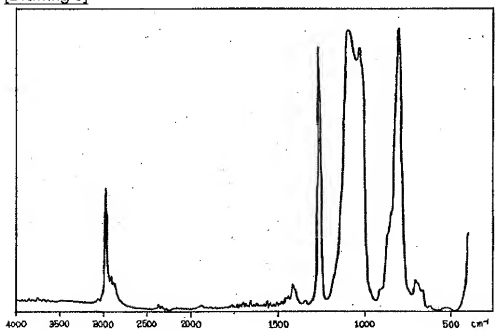
1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

DRAWINGS

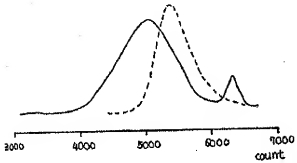
[Drawing 2]



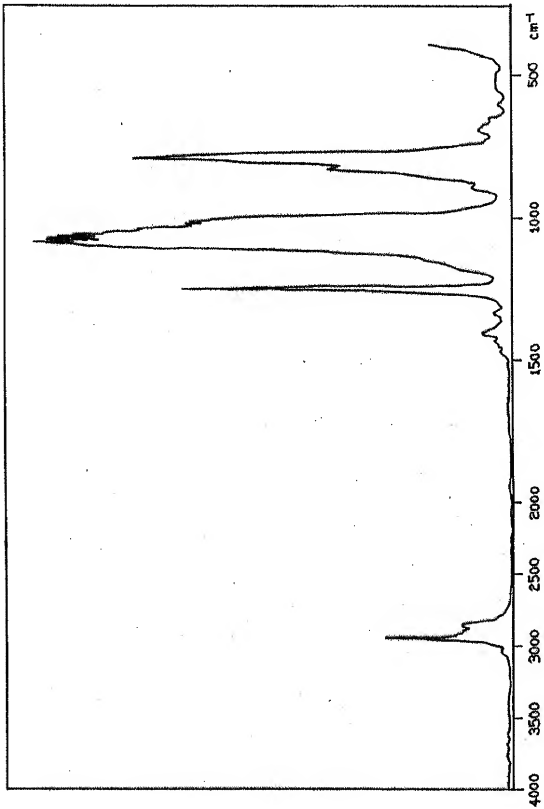
[Drawing 3]



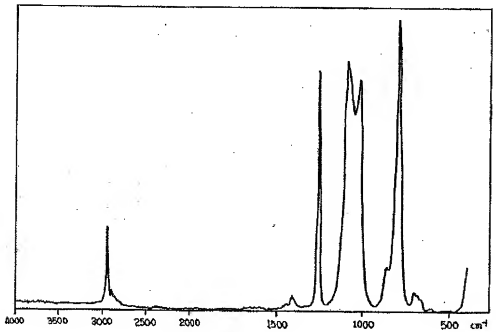
[Drawing 4]



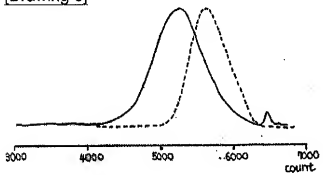
[Drawing 1]



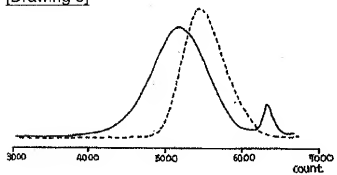
[Drawing 5]



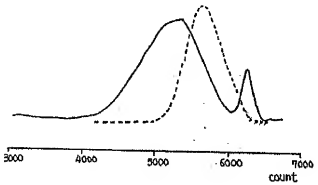
[Drawing 6]



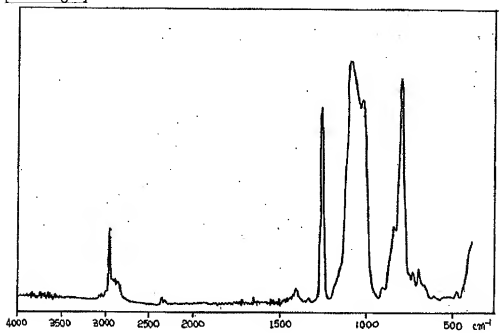
[Drawing 8]



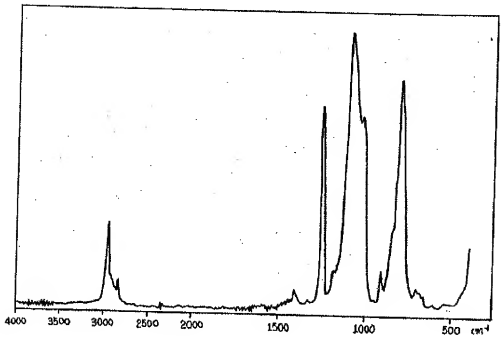
[Drawing 10]



[Drawing 7]



[Drawing 9]



[Translation done.]

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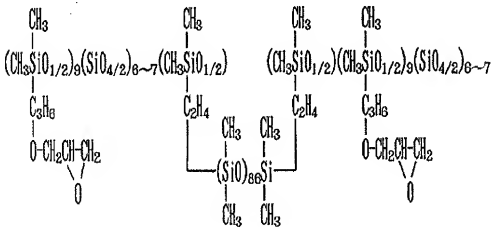
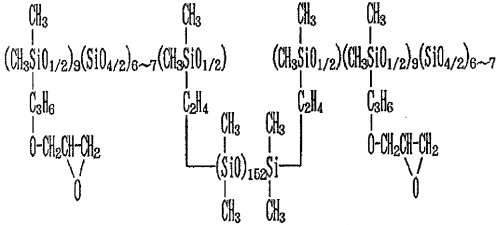
WRITTEN AMENDMENT

---------- [Written amendment]
[Filing date]October 16, Heisei 4
[Amendment 1]
[Document to be Amended]Specification
[Item(s) to be Amended]0027
[Method of Amendment]Change
[Proposed Amendment]
[0027]
[Formula 11]

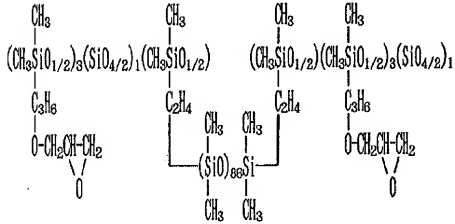


[Amendment 2]
[Document to be Amended]Specification
[Item(s) to be Amended]0032
[Method of Amendment]Change

[Proposed Amendment]
[0032]
[Formula 15]



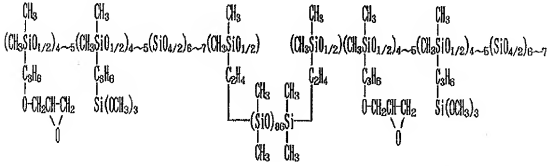
[Amendment 3]
[Document to be Amended]Specification
[Item(s) to be Amended]0037
[Method of Amendment]Change
[Proposed Amendment]
[0037]
[Formula 19]



[Amendment 4]
[Document to be Amended]Specification
[Item(s) to be Amended]0045
[Method of Amendment]Change
[Proposed Amendment]

[0045]

[Formula 26]



[Translation done.]

(19)日本国特許庁（ＪＰ）　(12) 公開特許公報（A）　(11)特許出願公開番号

特開平6－56999

(43)公開日　平成６年(1994)３月１日

(51)Int.Cl.[5]	識別記号	庁内整理番号	ＦＩ	技術表示箇所
Ｃ０８Ｇ　77/38	ＮＵＦ	8319－4Ｊ		

審査請求　未請求　請求項の数２(全 17 頁)

(21)出願番号　特願平4－229290

(22)出願日　平成４年(1992)８月５日

(71)出願人　000110077
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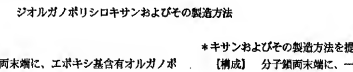
千葉県市原市千種海岸２番２　東レ・ダウコーニング・シリコーン株式会社研究開発本部内

(54)【発明の名称】　ジオルガノポリシロキサンおよびその製造方法

(57)【要約】
【目的】　分子鎖両末端に、エポキシ基含有オルガノポリシロキサン残基を有する、新規なジオルガノポリシロキサンおよびその製造方法を提供する。
【構成】　分子鎖両末端に、一般式：
【化１】



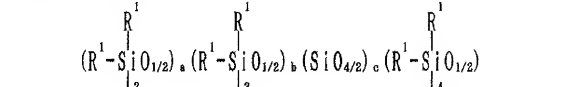
〔式中、R^1はアルケニル基を除く一価炭化水素基であり、R^2はアルケニル基を除く一価炭化水素基または水素原子であり、R^3はエポキシ基結合有機基またはアルコキシシリルアルキル基であり、ただし、R^3の内少なくとも１個はエポキシ基含有有機基であり、R^4は二価炭化水素基であり、またａは０または正数であり、ｂは正数であり、ｃは正数であり、かつａ／ｃは０～４の正数であり、ｂ／ｃは０．０５～４の正数であり、（ａ＋ｂ）／ｃは０．２～４の正数である。〕で表されるオルガノポリシロキサン残基を有するジオルガノポリシロキサンおよびその製造方法。

1　　2

〔特許請求の範囲〕

【請求項1】　分子鎖両末端に、一般式：

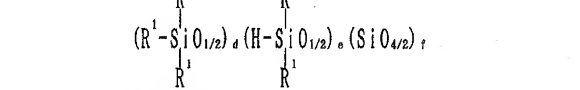
*【化1】



〔式中、R^1はアルケニル基を除く一価炭化水素基であり、R^2はアルケニル基を除く一価炭化水素基または水素原子であり、R^3はエポキシ基含有有機基またはアルコキシシリルアルキル基、ただし、R^3の内少なくとも1個はエポキシ基含有有機基であり、R^4は二価炭化水素基であり、またaは0またはは正数であり、bは正数であり、cは正数であり、かつa／cは0～4の正数であり、b／cは0．05～4の正数であり、（a＋b）／cは0．2～4の正数である。〕で表されるエポキシ基含有オルガノポリシロキサン残基を有するジオルガノポリシロキサン。

【請求項2】　(A)白金系触媒の存在下、(B)一般式：

【化2】



〔式中、R^1はアルケニル基を除く一価炭化水素基であり、またdは0または正数であり、eは正数であり、fは正数であり、かつd／fは0～4の正数であり、e／fは0．05～4の正数であり、（d＋e）／fは0．2～4の正数である。〕で表されるオルガノポリシロキサン、(C)エポキシ基と脂肪族不飽和結合を有する有機化合物、(D)分子鎖両末端にアルケニル基を有するジオルガノポリシロキサン｛(C)成分と(D)成分の添加量は、(B)成分中のケイ素原子結合水素原子1モルに対して、(C)成分と(D)成分に含まれる脂肪族不飽和結合のモル数が当量以上となる量である。｝および(E)任意量のアルコキシシリルアルケンを付加反応することを特徴とする請求項1記載のジオルガノポリシロキサンの製造方法。

【発明の詳細な説明】

【0001】

【産業上の利用分野】本発明は、ジオルガノポリシロキサンおよびその製造方法に関し、詳しくは、分子鎖両末端にエポキシ基含有オルガノポリシロキサン残基を有する、新規なジオルガノポリシロキサンおよびその製造方法に関する。

【0002】

【従来の技術】エポキシ基を有するジオルガノポリシロキサンは、エポキシ樹脂やフェノール樹脂等の熱硬化性有機樹脂に配合することにより、硬化後の硬化有機樹脂に対してジオルガノポリシロキサンの特徴である離型性、耐候性、柔軟性等の特性を付与し、さらに該硬化有機樹脂の内部応力を緩和することができる。

【0003】このようなエポキシ基を有するジオルガノポリシロキサンとしては、例えば、分子鎖側鎖にエポキシ基を有するジオルガノポリシロキサン（特開昭61－60726号公報参照）または分子鎖両末端にエポキシ基を有するジオルガノポリシロキサン（特開平2－69528号公報参照）が提案されている。

【0004】

【発明が解決しようとする問題点】しかし、特開昭61－60726号公報により提案されたジオルガノポリシロキサンは、その分子鎖側鎖に有するエポキシ基の反応性が低く、これをエポキシ樹脂やフェノール樹脂等の熱硬化性有機樹脂に配合すると、ジオルガノポリシロキサン中の未反応のエポキシ基により、得られた硬化有機樹脂の物理特性が経時的に変化するという問題があり、また特開平2－69528号公報により提案されたジオルガノポリシロキサンは、一分子中のエポキシ基が2個に限定されるという問題があった。

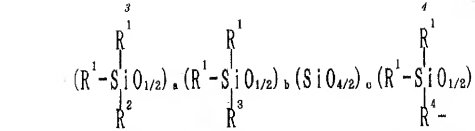
【0005】本発明者は、上記問題を解決するため鋭意努力した結果、本発明に到達した。

【0006】すなわち、本発明の目的は、分子鎖両末端にエポキシ基含有オルガノポリシロキサン残基を有する、新規なジオルガノポリシロキサンおよびその製造方法を提供することにある。

【0007】

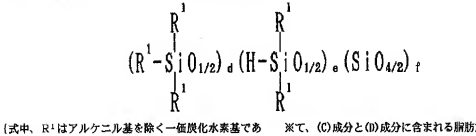
【問題点を解決するための手段およびその作用】本発明は、分子鎖両末端に、一般式：

【化3】



(式中、R^1はアルケニル基を除く一価炭化水素基であり、R^2はアルケニル基を除く一価炭化水素基または水素原子であり、R^3はエポキシ基含有有機基またはアルコキシシリルアルキル基、ただし、R^3の内少なくとも1個はエポキシ基含有有機基であり、R^4は二価炭化水素基であり、またaは0または正数であり、bは正数であり、cは正数であり、かつa／cは0～4の正数であり、b／cは0．05～4の正数であり、(a＋b)／cは0．2～4の正数である。)で表されるエポキシ基含有オルガノポリシロキサン残基を有するジオルガノポリシロキサン、および、(A)白金系触媒の存在下、(B)一般式：

【化4】

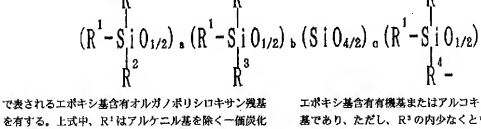


(式中、R^1はアルケニル基を除く一価炭化水素基であり、またdは0または正数であり、eは正数であり、fは正数であり、かつd／fは0～4の正数であり、e／fは0．05～4の正数であり、(d＋e)／fは0．2～4の正数である。)で表されるオルガノポリシロキサン、(C)エポキシ基と脂肪族不飽和結合を有する有機化合物、(D)分子鎖両末端にアルケニル基を有するジオルガノポリシロキサン、{(C)成分と(D)成分の添加量は、(B)成分中のケイ素原子結合水素原子1モルに対し※0.1～※10．0※て、(C)成分と(D)成分に含まれる脂肪族不飽和結合のモル数が当量以上となる量である。}および(E)　任意量のアルコキシシリルアルケンを付加反応することを特徴とするジオルガノポリシロキサンの製造方法に関する。

【0008】はじめに、本発明のジオルガノポリシロキサンについて詳細に説明する。

【0009】本発明のジオルガノポリシロキサンは、分子鎖両末端に、一般式：

【化5】



で表されるエポキシ基含有オルガノポリシロキサン残基を有する。上式中、R^1はアルケニル基を除く一価炭化水素基であり、具体的には、メチル基，エチル基，プロピル基，ブチル基，ペンチル基，ヘキシル基等のアルキル基；シクロペンチル基，シクロヘキシル基，シクロヘプチル基等のシクロアルキル基；フェニル基，トリル基，キシリル基等のアリール基；ベンジル基，フェネチル基，フェニルプロピル基等のアラルキル基；クロロメチル基，3，3，3－トリフルオロプロピル基等の置換アルキル基等の一価炭化水素基が例示される。また、R^2はアルケニル基を除く一価炭化水素基または水素原子であり、R^2の一価炭化水素基として、具体的には、前記と同様の一価炭化水素基が例示される。また、R^3はエポキシ基含有有機基またはアルコキシシリルアルキル基であり、ただし、R^3の内少なくとも1個はエポキシ基含有有機基である。R^3のエポキシ基含有有機基として、具体的には、グリシドキシエチル基，グリシドキシプロピル基，3，4－エポキシシクロヘキシルエチル基等のエポキシ基含有有機基が例示され、またR^3のアルコキシシリルアルキル基として、具体的には、トリメトキシシリルエチル基，トリメトキシシリルプロピル基，ジメトキシメチルシリルプロピル基，メトキシジメチルシリルプロピル基，トリエトキシシリルエチル基，トリプロポキシシリルプロピル基等のアルコキシシリルアルキル基が例示される。さらに、R^4は二価炭化水素基であり、具体的には、メチルメチレン基，エチレン基，メ

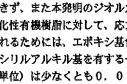
5　　6

チルエチレン基，プロピレン基，ブチレン基，ペンチレン基等が例示される。本発明のジオルガノポリシロキサンは，R^4基を介して上記エポキシ基含有オルガノポリシロキサン残基と結合している。

【0010】また、上式中、aはアルケニル基を除く一価炭化水素基またはケイ素原子結合水素原子を有する一官能性シロキサン単位（M単位）の数を示す0または正数であり、bはエポキシ基含有有機基またはアルコキシシリルアルキル基を有する一官能性シロキサン単位（M単位）の数を示す正数であり、cは四官能性シロキサン単位（Q単位）の数を示す正数であり、それぞれの比、a／cは0～4の正数であり、b／cは0．05～4の正数であり、かつ（a＋b）／cは0．2～4の正数である。これは、四官能性シロキサン単位（Q単位）1個に対して一官能性シロキサン単位（M単位）は4個をこえることはできず、また本発明のジオルガノポリシロキサンが、熱硬化性有機樹脂に対して、応力緩和効果および相溶性に優れるためには、エポキシ基含有有機基またはアルコキシシリルアルキル基を有する一官能性シロキサン単位（M単位）は少なくとも0．05個であることが必要であるからである。

【0011】本発明のジオルガノポリシロキサンは、分子鎖両末端にエポキシ基含有オルガノポリシロキサン残基を有するが、主鎖部分のジオルガノポリシロキサンは、特に限定されず、例えば、一般式：

【化6】



で表されるジオルガノポリシロキサンが挙げられる。上式中、R^1はアルケニル基を除く一価炭化水素基であり、具体的には、前記同様の一価炭化水素基が例示される。また、上式中、nは主鎖であるジオルガノポリシロキサンの重合度を示す正数であり、特に限定されない＊が、本発明のジオルガノポリシロキサンが熱硬化性有機樹脂に対して応力緩和効果および相溶性に優れるためには、nは1～500の範囲であることが好ましい。このような主鎖部分のジオルガノポリシロキサンとして、具体的には、ジメチルポリシロキサン，メチルエチルポリシロキサン，メチルフェニルポリシロキサン，ジメチルシロキサン・メチルフェニルシロキサン共重合体，ジメチルシロキサン・ジフェニルシロキサン共重合体，ジフェニルポリシロキサン等のジオルガノポリシロキサンが例示される。

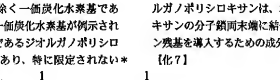
【0012】本発明のジオルガノポリシロキサンは、室温で液状または固体状であり、その分子量は特に限定されないが、これをエポキシ樹脂やフェノール樹脂等の熱硬化性有機樹脂に配合した場合，該有機樹脂との相溶性が良好であることから、本発明のジオルガノポリシロキサンの分子量は500～1，000，000の範囲であることが好ましい。

【0013】つぎに、本発明のジオルガノポリシロキサンの製造方法について説明する。

【0014】本発明の製造方法において、(A)成分の白金系触媒は、(B)成分中のケイ素原子結合水素原子と(C)成分、(D)成分および(E)成分中の脂肪族不飽和結合とを付加反応するための触媒である。(A)成分の白金系触媒は、通常、ヒドロシリル化付加反応触媒として使用されるものであれば特に限定されない。このような(A)成分の白金系触媒として、具体的には、塩化白金酸、塩化白金酸のアルコール溶液、白金とオレフィン類等の不飽和脂肪族炭化水素との錯体、白金とビニルシロキサンとの錯体、白金黒、白金担持の活性炭等が例示される。本発明の製造方法において、(A)成分の添加量は特に限定されず、通常の触媒量であり、具体的には、(B)成分に対して(A)成分中の白金金属として0．01～500ppmの範囲であることが好ましい。

【0015】本発明の製造方法において、(B)成分のオルガノポリシロキサンは、本発明のジオルガノポリシロキサンの分子鎖両末端に結合するオルガノポリシロキサン残基を導入するための成分であり、一般式：

【化7】



で表される。上式中、R^1はアルケニル基を除く一価炭化水素基であり、具体的には、メチル基，エチル基，プロピル基，ブチル基，ペンチル基，ヘキシル基等のアルキル基；シクロペンチル基，シクロヘキシル基，シクロヘプチル基等のシクロアルキル基；フェニル基，トリル基，キシリル基等のアリール基；ベンジル基，フェネチル基，フェニルプロピル基等のアラルキル基；クロロメチル基，3，3，3－トリフルオロプロピル基等の置換アルキル基等の一価炭化水素基が例示される。また、dはアルケニル基を除く一価炭化水素基を有する一官能性

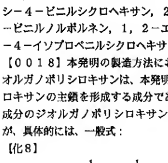
シロキサン単位（M単位）の数を示す0または正数であり、eはケイ素原子結合水素原子を有する一官能性シロキサン単位（M単位）の数を示す正数であり、fは四官能性シロキサン単位（Q単位）の数を示す正数であり、それぞれの比、d／fは0～4の正数であり、e／fは0．05～4の正数であり、かつ（d＋e）／fは0．2～4の正数である。これは、四官能性シロキサン単位（Q単位）1個に対して、一官能性シロキサン単位8M単位）は4個をこえることはできず、また本発明のジオルガノポリシロキサンが熱硬化性有機樹脂に対して反応性を有し、相溶性に優れるためには、ケイ素原子結合水素原子を有する一官能性シロキサン単位（M単位）は少なくとも0．05個であることが必要であるからである。

【0016】このような、(B)成分のオルガノポリシロキサンは、従来周知の方法により製造することができる。(B)成分の製造方法として、具体的には、テトラハロシランとモノハロシランを共加水分解する方法、テトラアルコキシシランとモノアルコキシシランを共加水分解する方法、テトラアルコキシシランとテトラオルガノジシロキサンを加水分解および再平衡化重合する方法等が例示され、好ましくは、塩酸水溶液中で、ヘキサオルガノジシロキサン、テトラオルガノジシロキサン、トリオルガノハロシランおよびジオルガノハロシランからなる群から選択される有機ケイ素化合物を攪拌しながら、テトラアルコキシシランを滴下する方法（特開昭61－195129号公報参照）である。

【0017】本発明の製造方法において、(C)成分のエポキシ基と脂肪族不飽和結合を有する有機化合物は、オルガノポリシロキサン残基にエポキシ基含有有機基を導入するための成分である。(C)成分のエポキシ基と脂肪族不飽和結合を有する有機化合物として、具体的には、ビニルグリシドキシエーテル，アリルグリシドキシエーテル，ブテニルグリシドキシエーテル，1，2－エポキシ－4－ビニルシクロヘキサン，2，3－エポキシ－5－ビニルノルボルネン，1，2－エポキシ－1－メチル－4－イソプロペニルシクロヘキサン等が例示される。

【0018】本発明の製造方法において、(D)成分のジオルガノポリシロキサンは、本発明のジオルガノポリシロキサンの主鎖を形成する成分である。このような(D)成分のジオルガノポリシロキサンは特に限定されないが、具体的には、一般式：

【化8】



（式中、R^1はアルケニル基を除く一価炭化水素基であり、R^4はアルケニル基であり、nは正数である。）で表される。上式中、R^1はアルケニル基を除く一価炭化水素基であり、具体的には、前記と同様の一価炭化水素基が例示される。また、R^6はアルケニル基であり、具体的には、ビニル基，アリル基，ブテニル基，ペンテニル基，ヘキセニル基，ヘプテニル基等が例示される。また、nはジオルガノポリシロキサンの重合度を示す正数であり、得られる本発明のジオルガノポリシロキサンが熱硬化性有機樹脂に対して応力緩和効果および相溶性に優れることから、nは1～5000の範囲の正数であることが好ましい。このような(D)成分のジオルガノポリシロキサンとして、具体的には、分子鎖両末端がジメチルビニルシロキシ基で封鎖されたジメチルポリシロキサン，分子鎖両末端がジメチルアリルシロキシ基で封鎖されたジメチルポリシロキサン，分子鎖両末端がジメチルヘキセニルシロキシ基で封鎖されたジメチルポリシロキサン，分子鎖両末端がジメチルビニルシロキシ基で封鎖されたメチルエチルポリシロキサン，分子鎖両末端がジメチルアリルシロキシ基で封鎖されたメチルエチルポリシロキサン，分子鎖両末端がメジメチルビニルシロキシ基で封鎖されたメチルフェニルポリシロキサン，分子鎖両末端がジメチルアリルシロキシ基で封鎖されたメチルフェニルポリシロキサン，分子鎖両末端がジメチルヘキセニルシロキシ基で封鎖されたメチルフェニルポリシロキサン，分子鎖両末端がジフェニルビニルシロキシ基で封鎖されたメチルフェニルポリシロキサン，分子鎖両末端がジメチルビニルシロキシ基で封鎖されたジメチルシロキサン・メチルフェニルシロキサン共重合体，分子鎖両末端がジメチルビニルシロキシ基で封鎖されたジメチルシロキサン・ジフェニルシロキサン共重合体，分子鎖両末端がジメチルアリルシロキシ基で封鎖されたジメチルシロキサン・ジフェニルシロキサン共重合体，分子鎖両末端がジメチルビニルシロキシ基で封鎖されたジフェニルメチルシロキサン等が例示される。

【0019】本発明の製造方法において、(C)成分と(D)成分の添加量は、(B)成分のオルガノポリシロキサン中のケイ素原子結合水素原子1モルに対して、(C)成分と(D)成分に含まれる脂肪族不飽和結合のモル数が当量以上となる量であることが必要である。また、(C)成分と(D)成分の添加量の比は任意であり、特に限定されない。

【0020】本発明の製造方法において、(E)成分のアルコキシシリルアルケンは、オルガノポリシロキサン残基にアルコキシシリルアルキル基を導入するための成分である。(E)成分のアルコキシシリルアルケンとして、具体的には、トリメトキシビニルシラン，トリエトキシビニルシラン，メチルジメトキシビニルシラン，アリルトリメトキシシラン，アリルメチルジエトキシシラン，メトキシジフェニルビニルシラン等が例示される。本発

明の製造方法において、(E)成分の添加量は任意であり、本発明のジオルガノポリシロキサンにアルコキシシリルアルキル基を導入する必要がある場合に、(C)成分と(D)成分と共に反応させることができる。本発明の製造方法において、(F)成分を添加する場合には、(B)成分中のケイ素原子結合水素原子１個に対して、(C)成分と(D)成分と(E)成分中の脂肪族不飽和結合の数が１個未満であれば、得られた本発明のジオルガノポリシロキサンは、分子鎖両末端に、ケイ素原子結合水素原子を一部有するオルガノポリシロキサン残基を有することになり、また、１個以上であれば、分子鎖両末端に、ケイ素原子結合水素原子を有しないオルガノポリシロキサン残基を有することになる。

【００２１】本発明の製造方法において、反応手順は特に限定されず、例えば、はじめに(A)成分と(B)成分を混合し、この系中に(C)成分と(D)成分を添加することによより、分子鎖両末端に、ケイ素原子原子結合水素原子とエポキシ基含有有機基とを有するオルガノポリシロキサン残基を有するジオルガノポリシロキサンを調製し、次いで、この系に(E)成分を添加することにより、分子鎖両末端に、エポキシ基含有有機基とアルコキシシリルアルキル基とを有するオルガノポリシロキサン残基を有するジオルガノポリシオキサンを調製することができ、また、初めに(A)成分と(D)成分を混合し、この系中に(B)成分を添加することにより、ケイ素原子結合水素原子とアルコキシシリルアルキル基とを有するオルガノポリシロキサンを調製し、次いで、この系に(C)成分と(D)成分を添加することにより、分子鎖両末端に、エポキシ基含有有機基とアルコキシシリルアルキル基とを有するオルガノポリシロキサン残基を有するジオルガノポリシロキサンを調製することができる。

【００２２】本発明の製造方法において、その反応温度は特に限定されず、付加反応を速やかに完結させるためには、反応温度は５０～１５０℃の範囲であることが好ましい。また、本発明の製造方法において、有機溶剤を使用することができる。本発明で使用できる有機溶剤と＊して、具体的には、トルエン，キシレン等の芳香族系有機溶剤；ヘキサン，ヘプタン，オクタン等の脂肪族系有機溶剤；アセトン，メチルエチルケトン等のケトン系有機溶剤等が例示される。このようにして製造された本発明のジオルガノポリシロキサンは、反応混合物として得られるが、静置することにより未反応のオルガノポリシロキサンと分離することができ、また本発明のオルガノポリシロキサンと未反応のオルガノポリシロキサンを有機溶媒に対する溶解度の差を利用して分離精製したり、ゲルパーミエーションクロマトグラフにより分離精製することができる。

【００２３】本発明のジオルガノポリシロキサンは、分子鎖両末端にエポキシ基含有オルガノポリシロキサン残基を有するので、エポキシ樹脂，フェノール樹脂，ポリイミド樹脂，ポリエステル樹脂，ポリアミド樹脂等の熱硬化性有機樹脂と反応させることにより、硬化後の硬化有機樹脂にジオルガノポリシロキサンの特徴である離型性、耐候性、柔軟性等の特性を付与することができ、また、硬化有機樹脂の内部応力を緩和することができる。

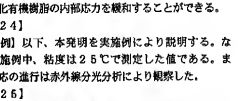
【００２４】

【実施例】以下、本発明を実施例により説明する。なお、実施例中、粘度は２５℃で測定した値である。また、反応の進行は赤外線分光分析により観察した。

【００２５】

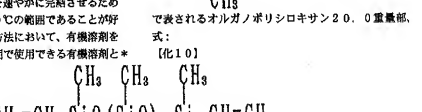
【実施例１】撹拌装置、還流冷却管および温度計付き５００ミリリットルの四つ口フラスコに、式：

【化９】



で表されるオルガノポリシロキサン２０．０重量部、式：

【化１０】



で表されるジメチルポリシロキサン２０．０重量部、アリルグリシジルエーテル３１．５重量部およびトルエン６０重量部を仕込み、加熱して系中の水分を共沸物として取り除き、窒素雰囲気下で冷却した。次に、この系中に２重量％－塩化白金酸のイソプロパノール溶液をスポイトにて１０滴滴下し、加熱撹拌し、８０℃で１．５時間加熱した後、室温まで冷却した。次に、モレキュラーシーブで脱水したアリルグリシジルエーテル１０重量部を添加し、再び１１０℃で２時間加熱した後、１２０℃で２mmHgの加熱減圧下で、トルエンおよび過剰のアリルグリシジルエーテルを除去し、褐色透明液体６２．８重量部を得た。

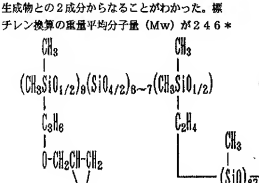
【００２６】得られた褐色透明液体は、エポキシ当量が３９０であり、粘度が７０４０センチポイズであった。また、得られた褐色透明液体を室温で１ヶ月放置したが、分離は観察されなかった。得られた褐色透明液体を

11　　12

赤外分光分析より測定したところ、Si－H結合による特性吸収は観察されなかった。また、得られた褐色透明液体をゲルパーミエーションクロマトグラフにより分析したところ、標準ポリスチレン換算の重量平均分子量（Mw）が24600、分散度（Mw／Mn）が1．76である生成物と標準ポリスチレン換算の重量平均分子量（Mw）が1480、分散度（Mw／Mn）が1．11である生成物との2成分からなることがわかった。標準ポリスチレン換算の重量平均分子量（Mw）が2460＊00、分散度（Mw／Mn）が1．76である生成物をゲルパーミエーションクロマトグラフにより分取し、これを^{1}H－核磁気共鳴分析、^{13}C－核磁気共鳴分析および^{29}Si－核磁気共鳴分析による構造解析を行ったところ、下式で表されるジオルガノポリシロキサンであることが確認された。

【0027】

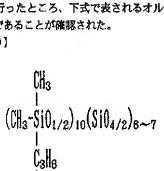
【化11】



【0028】また、標準ポリスチレン換算の重量平均分子量（Mw）が1480、分散度（Mw／Mn）が1．11である生成物をゲルパーミエーションクロマトグラフにより分取し、これを^{1}H－核磁気共鳴分析、^{13}C－核磁気共鳴分析および^{29}Si－核磁気共鳴分析による構造解析を行ったところ、下式で表されるオルガノポリシロキサンであることが確認された。

【0029】

【化12】

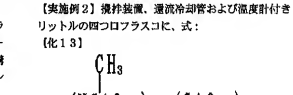


で表されるジメチルポリシロキサン219．2重量部、アリルグリシジルエーテル15．1重量部およびトルエン270．0重量部を仕込み、加熱して系中の水分を共沸物として取り除き、窒素雰囲気下で冷却した。次に、

※【0030】

【実施例2】撹拌装置、還流冷却管および温度計付き1リットルの四つ口フラスコに、式：

【化13】



で表されるオルガノポリシロキサン50．0重量部、式：

【化14】

で表されるオルガノポリシロキサン219．2重量部、アリルグリシジルエーテル15．1重量部およびトルエン270．0重量部を仕込み、加熱して系中の水分を共沸物として取り除き、窒素雰囲気下で冷却した。次に、この系中に2重量%－塩化白金酸のイソプロパノール溶液をスポイトにて10滴滴下し、加熱撹拌し、80℃で3時間加熱した後、室温まで冷却した。次に、モレキュラーシーブで脱水したアリルグリシジルエーテル50．

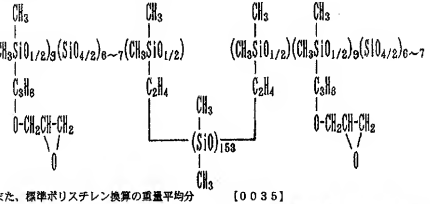
13　　14

0重量部を添加し、再び110℃で2時間加熱した後、120℃で2mmHgの加熱減圧下で、トルエンおよび過剰のアリルグリシジルエーテルを除去し、白濁液体316．6重量部を得た。

【0031】得られた白濁液体の粘度は、エポキシ当量が879であり、粘度が12800センチポイズであった。得られた白濁液体を室温で4ヶ月放置したが、分離は観察されなかった。得られた白濁液体を赤外線分光分析により測定したところ、Si－H結合による特性吸収は観察されなかった。また、得られた白濁液体をゲルパーミエーションクロマトグラフにより測定したところ、標準ポリスチレン換算の重量平均分子量（Mw）が53400、分散度（Mw／Mn）が2．44である生成物＊と標準ポリスチレン換算の重量平均分子量（Mw）が1540、分散度が（Mw／Mn）が1．12である生成物との2成分からなり、その重量比は93．2：6．7であった。標準ポリスチレン換算の重量平均分子量（Mw）が53400、分散度（Mw／Mn）が2．44である生成物をゲルパーミエーションクロマトグラフにより分取し、これを^{1}H－核磁気共鳴分析、^{13}C－核磁気共鳴分析および^{29}Si－核磁気共鳴分析による構造解析を行ったところ、下式で表されるジオルガノポリシロキサンであることが確認された。

【0032】

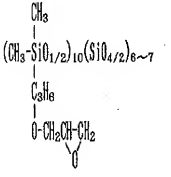
【化15】



【0033】また、標準ポリスチレン換算の重量平均分子量（Mw）が1540、分散度（Mw／Mn）が1．12である生成物をゲルパーミエーションクロマトグラフにより分取し、これを^{1}H－核磁気共鳴分析、^{13}C－核磁気共鳴分析および^{29}Si－核磁気共鳴分析による構造解析を行ったところ、下式で表されるオルガノポリシロキサンであることが確認された。

【0034】

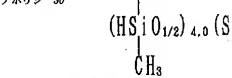
【化16】



【0035】

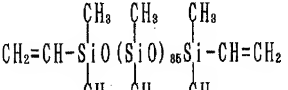
【実施例3】撹拌装置、還流冷却管および温度計付きの500ミリリットルの四つ口フラスコに、式：

【化17】



で表されるテトラキスジメチルシロキシシラン10重量部、式：

【化18】



15

で表されるジメチルポリシロキサン９８．５重量部、アリルグリシジルエーテル１０．４重量部およびトルエン１５０重量部を仕込み、加熱して系中の水分を共沸物として取り除き、窒素雰囲気下で冷却した。次に、この系中に２重量％－塩化白金酸のイソプロパノール溶液をスポイトにて５滴滴下し、加熱撹拌し、１００℃で０．５時間加熱した後、室温まで冷却した。次に、モレキュラーシーブで脱水したアリルグリシジルエーテル１０．９重量部を添加し、再び１１０℃で２時間加熱した後、１２０℃で２mmHgの加熱減圧下で、トルエンおよび過剰のアリルグリシジルエーテルを除去し、黄白色液体１１５．５重量部を得た。

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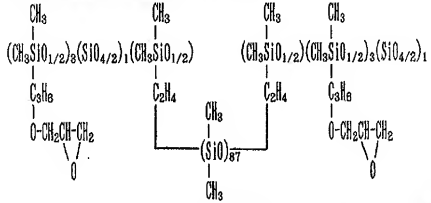
＊月放置したところ、わずかに白色沈澱の生成が観察された。上層の黄白色液体のエポキシ当量は１３００であった。上層の黄白色液体を赤外線分光分析により測定したところ、生成物のＳｉ－Ｈ結合による特性吸収がわずかに観察された。また、得られた黄色液体をゲルパーミエーションクロマトグラフにより分析したところ、標準ポリスチレン換算の重量平均分子量（Ｍｗ）が３１８０、分散度（Ｍｗ／Ｍｎ）が１．９７であった。この黄白色液体を、^{1}Ｈ－核磁気共鳴分析、^{13}Ｃ－核磁気共鳴分析および^{29}Ｓｉ－核磁気共鳴分析による構造解析を行ったところ、下式で表されるジオルガノポリシロキサンであることが確認された。

【００３６】得られた黄白色液体の粘度は１３４０センチポイズであった。得られた黄白色液体を室温で１０ヶ＊

【００３７】

【化１９】

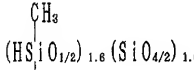


※で表されるオルガノポリシロキサン４０重量部、式：

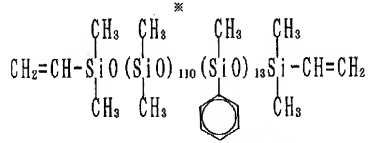
【００３８】

【実施例４】撹拌装置、還流冷却管および温度計付きの５００ミリリットルの四つ口フラスコに、式：

【化２０】



【化２１】



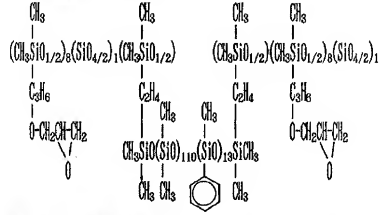
で表されるジメチルシロキサン・メチルフェニルシロキサン共重合体１２７．８重量部、アリルグリシジルエーテル３７．０重量部およびトルエン８０重量部を仕込み、加熱して系中の水分を共沸物として取り除き、窒素雰囲気下で冷却した。次に、この系中に２重量％－塩化白金酸のイソプロパノール溶液をスポイトにて１０滴滴下し、加熱撹拌し、１２０℃で１．５時間加熱した後、室温まで冷却した。次に、モレキュラーシーブで脱水したアリルグリシジルエーテル１１．５重量部を添加し、再び１２０℃で１時間加熱した後、１２０℃で２mmHgの加熱減圧下で、トルエンおよび過剰のアリルグリシジルエーテルを除去し、薄茶透明液体２０５．９重量部を得

た。

【0039】得られた薄茶透明液体の粘度は10000センチポイズであった。得られた薄茶透明液体を室温で4ヶ月放置したところ、上層に茶色透明液体、下層に茶色不透明液体とに分離し、その重量比は8：1であった。上層の薄茶透明液体をゲルパーミエーションクロマトグラフにより分析したところ、標準ポリスチレン換算の重量平均分子量（Mw）が39500、分散度（Mw／Mn）が2．12である生成物と標準ポリスチレン換算の重量平均分子量（Mw）が1380、分散度（Mw／Mn）が1．06である生成物との2成分からなり、＊その重量比は95．4：4．6であった。標準ポリスチレン換算の重量平均分子量（Mw）が39500、分散度（Mw／Mn）が2．12である生成物をゲルパーミエーションクロマトグラフにより分取し、これを^{1}H－核磁気共鳴分析、^{13}C－核磁気共鳴分析および^{29}Si－核磁気共鳴分析による構造解析を行ったところ、下式で表されるジオルガノポリシロキサンであることが確認された。

【0040】

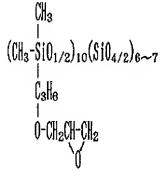
【化22】



【0041】また、標準ポリスチレン換算の重量平均分子量（Mw）が1380、分散度（Mw／Mn）が1．06である生成物をゲルパーミエーションクロマトグラフにより分取し、これを^{1}H－核磁気共鳴分析、^{13}C－核磁気共鳴分析および^{29}Si－核磁気共鳴分析による構造解析を行ったところ、下式で表されるオルガノポリシロキサンであることが確認された。

【0042】

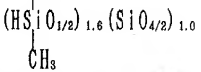
【化23】



【0043】

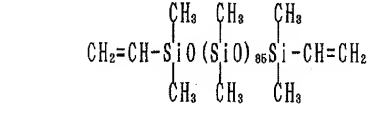
【実施例5】撹拌装置、還流冷却管および温度計付き1リットル四つ口フラスコに、式：

【化24】



で表されるオルガノポリシロキサン50重量部、式：

【化25】

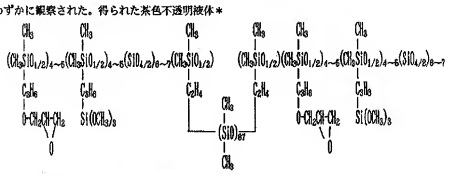


で表されるジメチルポリシロキサン１３１．８重量部、アリルグリシジルエーテル１５．２重量部、アリルトリメトキシシラン２１．４重量部およびトルエン２００重量部を仕込み、加熱して系中の水分を共沸物として取り除き、窒素雰囲気下で冷却した。次に、この系中に２重量％－塩化白金酸のイソプロパノール溶液をスポイトにて１０滴滴下し、加熱撹拌し、１２０℃で１時間加熱し、室温まで冷却した。次に、モレキュラシーブで脱水したアリルグリシジルエーテル１５．１重量部とアリルトリメトキシシラン２１．４重量部とを添加し、再び１１０℃で２時間加熱した後、１２０℃で２mmHgの加熱減圧下で、トルエンおよび未反応のアリルグリシジルエーテルとアリルトリメトキシシランとを除去し、茶色不透明液体２３５．４重量部を得た。

【００４４】得られた茶色不透明液体は１１５℃以上では茶色透明であった。得られた茶色不透明液体の粘度は２８００センチポイズであった。得られた茶色不透明液体を赤外線分光分析したところ、Ｓｉ－Ｈ結合による特性吸収がわずかに観察された。得られた茶色不透明液体＊を室温で５ヶ月放置したところ、上層に白濁液体、下層に茶色透明液体とに分離し、その重量比は１８：１であった。上層の白濁液体をゲルパーミエーションクロマトグラフにより分析したところ、標準ポリスチレン換算の重量平均分子量（Ｍｗ）が３０３００、分散度（Ｍｗ／Ｍｎ）が２．２１である生成物と標準ポリスチレン換算の重量平均分子量（Ｍｗ）が１９１０、分散度（Ｍｗ／Ｍｎ）が１．０７である生成物との２成分からなり、その重量比は９０．８：９．２であった。標準ポリスチレン換算の重量平均分子量（Ｍｗ）が３０３００、分散度（Ｍｗ／Ｍｎ）が２．２１である生成物をゲルパーミエーションクロマトグラフにより分取し、これを^{1}Ｈ－核磁気共鳴分析、^{13}Ｃ－核磁気共鳴分析および^{29}Ｓｉ－核磁気共鳴分析による構造解析を行ったところ、下式で表されるジオルガノポリシロキサンであることが確認された。

【００４５】

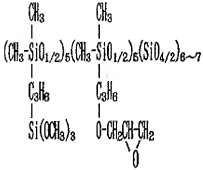
【化２６】



【００４６】また、標準ポリスチレン換算の重量平均分子量（Ｍｗ）が１９１０、分散度（Ｍｗ／Ｍｎ）が１．０７である生成物をゲルパーミエーションクロマトグラフにより分取し、これを^{1}Ｈ－核磁気共鳴分析、^{13}Ｃ－核磁気共鳴分析および^{29}Ｓｉ－核磁気共鳴分析による構造解析を行ったところ、下式で表されるオルガノポリシロキサンであることが確認された。

【００４７】

【化２７】



【００４８】

【発明の効果】本発明のジオルガノポリシロキサンは、分子鎖両末端に、エポキシ基含有オルガノポリシロキサン残基を有する、新規なジオルガノポリシロキサンであり、また本発明の製造方法は、このような新規なジオルガノポリシロキサンを製造できるという特徴を有する。

【図面の簡単な説明】

【図１】実施例１で調製したジオルガノポリシロキサンの赤外線分光分析チャートである。

【図２】実施例１で調製したジオルガノポリシロキサンのゲルパーミエーションクロマトグラフチャートである。なお、点線は原料のジメチルポリシロキサンを示し、実線は得られた褐色透明液体を示す。

【図３】実施例２で調製したジオルガノポリシロキサンの赤外線分光分析チャートである。

【図４】実施例２で調製したジオルガノポリシロキサンのゲルパーミエーションクロマトグラフチャートである。なお、点線は原料のジメチルポリシロキサンを示し、実線は得られた白濁液体を示す。

【図５】実施例３で調製したジオルガノポリシロキサンの赤外線分光分析チャートである。

【図６】実施例３で調製したジオルガノポリシロキサン

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のゲルパーミエーションクロマトグラフチャートである。なお、点線は原料のジメチルポリシロキサンを示し、実線は黄白色液体を示す。

【図７】実施例４で調製したジオルガノポリシロキサンの赤外線分光分析チャートである。

【図８】実施例４で調製したジオルガノポリシロキサンのゲルパーミエーションクロマトグラフチャートである。なお、点線は原料のジメチルシロキサン・メチルフェニルシロキサン共重合体を示し、実線は得られた淡茶透明液体を示す。

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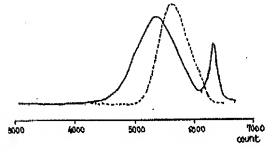
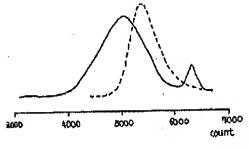
【図９】実施例５で調製したジオルガノポリシロキサンの赤外線分光分析チャートである。

【図１０】実施例５で調製したジオルガノポリシロキサンのゲルパーミエーションクロマトグラフチャートである。なお、点線は原料のジメチルポリシロキサンを示し、実線は得られた茶色不透明液体を示す。

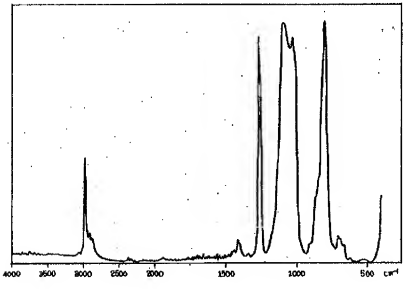
【図２】



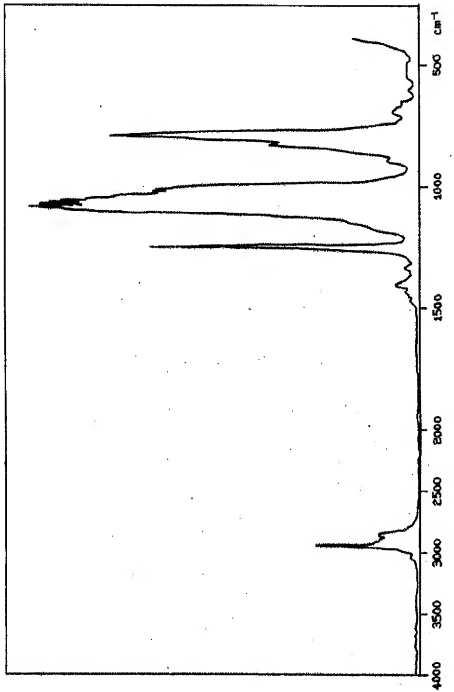
【図４】



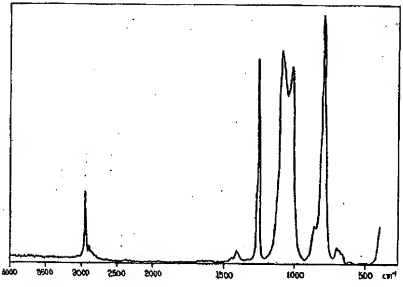
【図３】



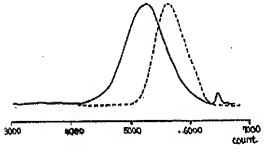
【図1】



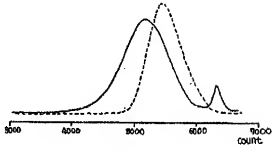
【図5】


4000
3500
3000
2500
2000
1500
1000
500
cm⁻¹

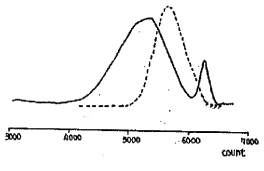
【図6】


3000
4000
5000
6000
7000
count

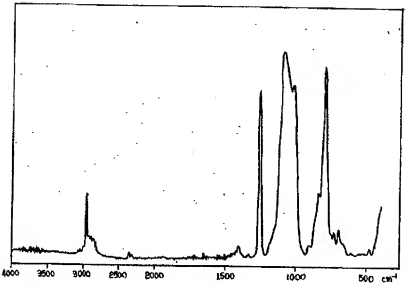
【図8】


3000
4000
5000
6000
7000
count

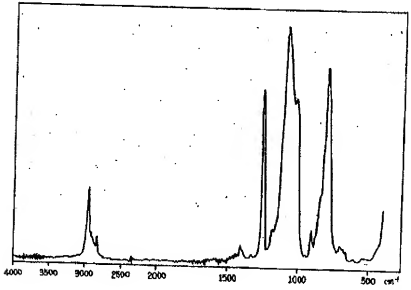
【図10】


3000
4000
5000
6000
7000
count

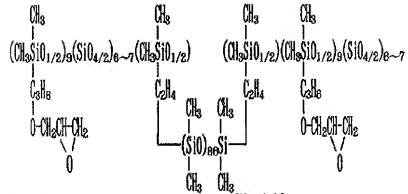
【図7】



【図9】

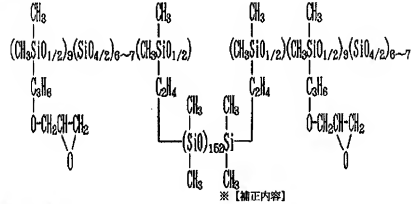


【手続補正書】
【提出日】平成４年１０月１６日
【手続補正１】
【補正対象書類名】明細書
【補正対象項目名】００２７
【補正方法】変更
【補正内容】
【００２７】
【化１１】



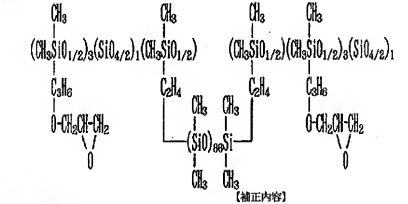
【手続補正2】
【補正対象書類名】明細書
【補正対象項目名】００３２
【補正方法】変更

*【補正内容】
【００３２】
【化１５】



【手続補正3】
【補正対象書類名】明細書
【補正対象項目名】００３７
【補正方法】変更

※【補正内容】
【００３７】
【化１９】



【手続補正4】
【補正対象書類名】明細書
【補正対象項目名】００４５
【補正方法】変更

【補正内容】
【００４５】
【化２６】